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I. *Notes on Corpuscular Radiation excited by X-Rays.* By
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THE recent important experimental work of M. de Broglie, of Whiddington, and of Shearer on the corpuscular radiation emitted from substances exposed to X-rays, emphasizes the need of further quantitative measurements upon radiation of this type. It will, however, be an advantage to recall the results of energy measurements which have already been made, for these appear to possess a significance which cannot be overlooked in a complete study of the subject. We propose therefore to give a brief account of these earlier experiments which led us to undertake the investigations described later.

The *maximum* velocity of emission of the electrons from metal plates was shown by Cooksey and Innes to be a function only of the penetrating power (or frequency) of the exciting radiation. Later it was assumed that it was given by the relation $\frac{1}{2}mv^2 = hn$: hence the frequency (n), and wave-length of the X-radiation was found. The method was later justified by the sufficiently close agreement with the wave-length determinations made by the interference method.

Accurate measurements show no appreciable variation in the *maximum* velocities of emission from various substances, and it is certain that for these $\frac{1}{2}mv^2$ differs little from hn .

* Communicated by the Authors.

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Shortly after the discovery of the characteristic X-radiations, however, Barkla* had observed the large sudden increase in the ionization produced in a gas, and Sadler† the increase in electronic emission from a metal plate when the primary radiation traversing these passed the critical frequency essential to the emission of a characteristic X-radiation in each. (One of us later pointed out that the electrons of the corpuscular radiation were emitted in clearly defined groups, each group being associated with a characteristic X-radiation from the substance. Thus a substance traversed by X-rays emits distinct groups of electrons constituting the K, L, M, etc. corpuscular radiations (producing K, L, M, etc. ionizations if the substance is in a gaseous form), associated with the emission of K, L, M, etc. characteristic radiations. The question naturally arose as to whether or not the velocity of emission of an electron from the parent atom depended upon the group of which the electron was a member, that is, upon the particular characteristic radiation with which it was associated.

As the energy of electrons ejected by an X-radiation of frequency n does not range continuously from hn downwards‡, the only alternatives which appear to have any theoretical probability are that the energy of escape from the parent atom is approximately hn , or that it is hn diminished by hn_k , hn_l , hn_m (say), this latter quantity being dependent on the particular group to which the ejected electron belongs. Thus the energy of a K electron—by which we mean an electron emitted in association only with the K characteristic radiation, whatever its origin—might be $h(n-n_k)$ where n_k is the critical absorption frequency in the substance for the K radiations,—or at any rate something near to that.

It is, however, quite a simple matter to decide experimentally between these *if they are the only two alternatives*. Experiments have been undertaken with that purpose, and other experimental results may be shown to furnish evidence on the same point. These experiments have been of two kinds in which the substance used has been in the form of (1) a gas, (2) a solid plate. In the case of gases traversed by X-rays, the energy of corpuscular emission has been measured by the ionization produced by the electrons in

* 'Nature,' April 15, 1909; Camb. Phil. Soc. Proc. May 1909; Phil. Mag. August 1910.

† Phil. Mag. March 1910.

‡ See C. T. R. Wilson's photographs.

the gas itself. Such measurements give the total energy without the necessity for any correction due to absorption. The energy of emission of electrons from plates exposed to X-rays has been measured by the ionization produced in a gas (usually air) just outside the surface. Such measurements, unless they are merely relative, involve a calculation of absorption based on somewhat questionable assumptions, and they give no indication of slowly moving electrons. But a comparison of these measurements both among themselves and with those obtained in experiments on gases lead to important conclusions.

We will first consider the results of experiments upon gases, as these are the more consistent; their interpretation is also less open to question.

GAS EXPERIMENTS.

The first application of ionization experiments to the measurement of the energy of corpuscular radiation was made by Barkla and Philpot*. This led at once to the conclusion that when a beam of X-rays is absorbed in a substance and little energy is re-emitted as characteristic radiation, the energy of the corpuscular radiation is approximately independent of the substance. In other words, the energy of the corpuscular radiation excited by an X-ray beam is proportional to the energy of the X-radiation absorbed whatever the absorbing substance—provided no appreciable amount of energy is re-emitted as fluorescent (characteristic) radiation. The condition may be otherwise expressed as: “provided the frequency (n) of the primary radiation is much greater than that (n_k or n_l) of any characteristic radiation excited in the absorbing substance.” It should be noticed that this was found to be true (with a maximum variation of only about 7 per cent.) for gases containing elements of atomic weight as high as 127 (iodine), and that in some cases the K corpuscular radiation was emitted, in others not. It is tolerably certain, then, that it is perfectly general. On either of the two suggested alternatives—that $E = hn$, or $E = h(n - n_k)$ —this would imply that under these conditions the number of electrons emitted is (approximately) independent of the absorbing substance—which is the form of the conclusion as stated in the original paper.

The interesting question then arose as to the energy

* Phil. Mag. June 1913.

of corpuscular radiation when n is only slightly greater than n_k and the characteristic X-radiation is excited in considerable intensity in the substance traversed by the primary beam. We already had data on this point, for Barkla has found* the sudden increase in ionization in C_2H_5Br when the frequency n of the ionizing radiation passed beyond the critical frequency (n_k) of bromine. The results are shown in Table I., where column 1 gives the ionizing radiations used, column 2 the wave-length of the α_1 constituent of this K radiation, column 3 the observed ionization in C_2H_5Br compared with that in an equal short path in air at the same pressure. With the purpose of obtaining accurate data in the critical region, the experiments were later performed in an entirely different way and with great care†, and the results given in column 4 were obtained. (In the first set the C_2H_5Br was mixed with air; in the later one the C_2H_5Br was pure.) The agreement between the two is quite close and leaves no doubt of the substantial accuracy of the relative ionizations.

TABLE I.

(1)	(2)	(3)	(4)
Radiation used.	Wave-length of $K\alpha_1$ constituents.	Ioniz. coeff. in C_2H_5Br Ioniz. coeff. in air	As (3).
Fe K radiation	1.932×10^{-8} cm.	x	x
to	to		
Br K radiation	1.035×10^{-8} cm.	x	x
.....			
Sr K radiation	$.871 \times 10^{-8}$ cm.	$3.5 \times x$	$3.3 \times x$
Mo "	.710 "	$4.4 \times x$	$4.4 \times x$
Ag "	.562 "	$5.1 \times x$	$5.6 \times x$
Sn "	.487 "	$5.8 \times x$	$6.0(7.9) \times x$
Sb "	.468 "	$5.5 \times x$	
Ce "	.355 "	$6.8(9.5) \times x$

The results show that as the frequency of the radiation passing through C_2H_5Br is increased, the ionization coefficient remains quite normal, being a constant (x) times that in air for instance, until the ionizing radiation has a frequency greater than the critical frequency for Br. Then there is a sudden and large rise in the ionization coefficient. How sudden this is was not shown by these

* Phil. Mag. August 1910.

† Bakerian Lecture 1916, Phil. Trans. 1917.

experiments, but when Sr "K" radiation was used, with wave-lengths about 16 per cent. shorter than the wave-lengths of corresponding radiations from Br, the ionization in the C_2H_5Br had increased to 3.5 times the normal value.

Again, confirmation of these results is obtained by a comparison with Beatty's values obtained for the ionization in SeH_2 and shown in Table II. The corresponding columns 1, 2, and 3 have the same meaning as in Table I.

TABLE II.

(1)	(2)	(3)
Radiation used,	Wave-lengths of	Ioniz. coeff. in SeH_2
	$K\alpha_1$ constituents.	Ioniz. coeff. in air
Fe K radiation	1.932×10^{-8} cm.	y
to	to	
Se K radiation	1.104×10^{-8} cm.	y
.		
Sr K radiation	$.871 \times 10^{-8}$ cm.	$4.1 \times y$
Mo "	$.710$ "	$6.3 \times y$
Ag "	$.562$ "	$7.7 \times y$
Sn "	$.487$ "	$8.3 \times y$
I "	$.437$ "	$9.5 \times y$

Selenium has a lower, critical frequency than Br; the magnitude of the increase in ionization is, however, almost exactly as found for bromine under corresponding conditions.

Now the critical absorption wave-length in Br is $.916 \text{ \AA.U.}$ according to de Broglie, or $.9179 \text{ \AA.U.}$ according to Duane. We thus see that when the frequency of the ionizing radiation (Sr K radiation) is in the main about 5 per cent. greater, the increase in ionization is 2.5 times the "normal" ionization—i. e., the K ionization is 2.5 times the L, M, N etc. ionizations together.

Considering now the two alternatives mentioned above, if $\frac{1}{2}mv^2 = hn$ and these K electrons thus move with approximately the same velocity as the L, M, and N electrons, there are 2.5 times as many ejected K electrons as ejected L, M, N, etc. electrons. But if the K electrons move with the velocity given by $\frac{1}{2}mv^2 = h(n - n_k)$, then the number of K electrons ejected is more than 30 times as great as the L, M, N electrons together.

Now if the energy of each electron is assumed to be hn , we arrive at the very simple and satisfactory conclusion that one electron is ejected in association with each quantum

of characteristic radiation *. This relation holds very closely not only when n is just greater than n_k , but also when it is much greater.

On the other hand, on the hypothesis that $\frac{1}{2}mv^2 = h(n - n_k)$ there must be many more, say roughly 10 "K" electrons, for each quantum of K characteristic radiation from bromine; and this number steadily diminishes with an increase in n . If this were the case, we should be led to one of two alternative conclusions:—either that one quantum of characteristic radiation is emitted for only one electron in every ten say, or that the characteristic radiation is not emitted in quanta, but in small fractions of a quantum. All the evidence is against the latter assumption; no one even suggests it. Neither is there any support for the former supposition—that the emission of characteristic radiation is only an occasional accompaniment of the emission of K electrons. That would be contrary to the accepted quantum theory of radiation and to the hypothesis which demands that the energy of ejection shall be $(hn - n_k)$.

Briefly, then, if the K electrons are ejected from the atom with the energy hn , there is one electron ejected for from two to one quantum of primary radiation absorbed; there is one electron ejected for each quantum of K characteristic radiation emitted, not only when n is just greater than n_k but when it becomes much greater.

On the other hand, if the energy of ejection be $h(n - n_k)$ these electrons are many times more numerous than the number of quanta of primary radiation absorbed, or than the number of quanta of characteristic K radiation emitted in association with them. Also the magnitude of their excess varies with the frequency n of the primary radiation. This is all contrary to the assumption necessary to explain the energy $h(n - n_k)$ at all!

This, however, does not show that *some* of the K electrons are not emitted with energy $h(n - n_k)$. There might conceivably be the required number of such electrons when n is just greater than n_k , and in addition an approximately equal number of swiftly moving electrons of energy hn . But such an assumption would mean, on this view, that the K group consisted of electrons both from the K level and from other—say L, M, and N levels.

It must be remembered, however, that no K electron is emitted unless $n > n_k$, *i. e.* this condition applies to *all*

* Barkla, Bakerian Lecture 1916.

electrons in the K group; so if some of these electrons are ejected from L, M, or N levels, it must be as a consequence of the ejection of electrons from the K level—that is, they must be ejected from the same atom. In other words, two electrons in the same atom would absorb one quantum of primary radiation, first the K electron, then an L, M, or N electron. This is highly improbable on any theory yet put forward, but is not inconceivable.

The following conclusions, which can hardly be disputed, may be drawn from the ionization experiments considered alone :—

The K ionization is *not* produced simply or even principally by electrons with energy $h(n-n_k)$. The K ionization *may be* produced by electrons with energy hn ,—indeed, if we assume that the K ionization is principally by such electrons, then we find that one quantum of K characteristic radiation is emitted for each electron.

While there is a possibility that many K electrons are emitted with energy $h(n-n_k)$, no suggested theory which takes them into consideration seems capable of explaining the K ionization quantitatively.

PLATE EXPERIMENTS.

The experimental results (published by a number of observers) on the corpuscular emission from plates seem also to indicate unquestionably that the vast majority of the K electrons (viz. those electrons emitted in association with K characteristic radiation whatever their origin) have substantially the same velocity as the other (L, M, N, ...) electrons ejected by the same primary radiation.

The evidence is of two kinds: the first based on observations of the *increase* in electronic emission when n exceeds n_k , the second based on measurements of the *total energy* (ionizing power) of the electrons.

The K increase of electronic emission.

SADLER: Thus Sadler * records something like a twenty-fold increase in the energy of corpuscular radiation emitted from a metal plate when the frequency of the primary radiation falling upon it is raised above that necessary to excite the K characteristic radiation. This is shown when Ni radiation (K) falls on Fe and when As radiation falls on Cu. (For wave-lengths see Table III.) Yet the

* Phil. Mag. March 1910.

absorbability of the corpuscular radiation (principally K electrons) is quite normal, following the same law as for the L, M, N electrons ejected from other substances by Ni and As radiations respectively.

TABLE III.

Wave-lengths of K radiations. (Unit= 10^{-8} cm.)
(From Siegbahn.)

	β_2	β_1	α_1	α_2
Fe	1.741	1.753	1.932	1.9366
Co	1.606	1.617	1.786	1.790
Ni	1.484	1.497	1.655	1.659
Cu	1.377	1.389	1.537	1.541
Zn	1.279	1.293	1.432	1.436
As	1.038	1.052	1.173	1.177
Se993	1.104	1.109
Br914	.929	1.035	1.04
Sr767	.779	.871	.876
Mo633	.710	.714
Ag491	.501	.562	.567
Sn432	.487	.490
Sb408	.416	.468	.472
Ce314	.355	.360

While for certain reasons these results are not altogether satisfactory, they must be very strangely in error if they do not show that the K electrons emerging from the plate move with substantially the same velocity as the L, M and other electrons. On the other hand, the increase in the energy of corpuscular emission observed by Sadler is certainly enormously larger than we have ever obtained from other elements—(see later)—and is difficult to account for on the basis of only an 8-fold increase in absorption. The absolute energy measurement, too, does not agree with that of other observers.

BRAGG: Again, though W. H. Bragg did not undertake a systematic investigation of the point, a fragment of the results of experiments by Bragg and Porter* indicates the sudden large increase in the corpuscular emission from a plate of zinc when the primary radiation was only just sufficiently penetrating to excite the K characteristic

* Proc. Roy. Soc. 1911.

radiation. Thus when Zn radiation fell upon Zn, the corpuscular emission was only $\cdot 33$ of that from Fe exposed to the same radiation; but when As radiation was used, the emission from Zn became $1\cdot 28$ times as great as that from Fe. That is, the corpuscular emission increased in the ratio $1:3\cdot 84$ when the K characteristic radiation was excited in Zn.

Or comparing with the emission of electrons from Ni, the sudden increase in the emission of electrons from Zn is given by the ratio $1:3\cdot 80$.

This meant that the K electrons emerging from the Zn plate have nearly three times ($2\cdot 8$) the energy of the L, M, N electrons, when the exciting radiation (As "K" radiation) has a frequency only about 20 per cent. greater than the frequency of the corresponding radiation from Zn, and the bulk of the exciting radiations has a frequency only about 10 per cent. greater than the critical absorption-frequency for Zn.

The increase is very much smaller than that recorded by Sadler, but it has every appearance of being of the right order of magnitude. The observations appear more consistent than Sadler's, and this isolated result agrees very closely with the sudden increase previously observed by us in the ionization in ethyl bromide, already referred to, when the frequency of the ionizing radiation was correspondingly greater than the characteristic frequency for bromine.

BEATTY: Further, though Beatty* does not show the variation in the energy of emission of electrons from a plate when n passes through this critical value n_k , his measure of this energy when n is greater than n_k (accounting for about half the K absorption in addition to the L, M, N absorptions) implies an increase of corpuscular emission as n passes n_k , of the magnitude found in ionization experiments, and indicated by the plate experiments of Bragg and Porter.

BARKLA & SHEARER: The unsatisfactory nature of Sadler's results and the fragmentary nature of Bragg's (the whole argument being dependent on a single measurement) led Barkla and Shearer to examine the absorption of the K electrons. It was thought that when the frequency n of the exciting radiation was only slightly greater than n_k the critical absorption frequency in the element experimented upon, a decided loss of energy such as would

* Proc. Roy. Soc. 1911.

be expressed by the equation $\frac{1}{2}mv^2 = h(n - n_k)$ might be observed. In these experiments, however, the K electrons, *i. e.* those electrons associated with the emission of K characteristic radiation as distinct from other electrons, produced effects much smaller than had been expected from the results of Sadler, smaller even than the effect recorded by Bragg, and smaller than that shown by measurements of ionization. The *increase* in the energy of the corpuscular emission when the characteristic radiation was excited in the metal plate was only of the order of 100 per cent., *i. e.* the whole corpuscular emission was only about doubled. However, measurement showed that the difference between these additional K electrons as they emerged from the plate and the other electrons (L, M, N electrons) was in one case certainly very small, and in the other could not be detected at all.

The principal point which was regarded as established was that the K electrons which emerged from the metal plate were electrons whose maximum energy was given by hn approximately and not by $h(n - n_k)$. Also that the distribution of energy among the whole group was very similar to that among the other electrons.

These experiments thus showed that many of the K electrons had the whole energy of a quantum, or something very near to the full energy of a quantum, of primary radiation. But they did not indicate, as did the experiments above referred to, that the energy of these was approximately the whole energy of the corpuscular radiation. As far as these experiments went, there appeared the possibility of other more slowly moving electrons. These could not have been detected.

Energy Measurements.

The question as to whether the K electrons, many of which are evidently emitted with approximately, if not accurately, the energy hn of a full quantum of the primary radiation, constitute the whole of the K corpuscular radiation, was first investigated by Barkla* in a comparison of the ionization observed in C_2H_5Br when traversed by Ag K rays, with that calculated as produced by the swift electrons, the data for the latter being obtained from Sadler's experiments on corpuscular radiation from plates. The results showed that these corpuscles accounted for less than half of the total K ionization, indicating the possibility of other more

* Phil. Mag. August 1910.

slowly moving K electrons. If, however, we use Beatty's data obtained later for the corpuscular emission from selenium, it appears that approximately all the ionization is by such swiftly moving electrons.

Beatty shortly afterwards used data agreeing with Barkla's for the ionization, but values for the corpuscular emission about 2.4 times that observed by Sadler, and found that approximately all the ionization observed in SeH_2 was produced by the electrons such as were observed from a plate of selenium. Making a correction which we have previously pointed out, the observed and calculated values agree more closely than Beatty thought. Thus when Sr, Mo, Ag, Sn, and I radiations (K series) were used the rapidly moving corpuscles accounted for 120, 87, 84, 86, and 103 per cent. respectively of the ionization actually observed in SeH_2 , though this was almost entirely K ionization. There is here no room for an appreciable amount of corpuscular radiation of any other type.

It would perhaps be easy to attach too much importance to agreement of this kind, for the calculation depends too closely on so-called coefficients of absorption of corpuscular radiations in the material from which they are emitted. Such calculations as have been made, however, indicated that a large portion of the K corpuscular radiation consists of electrons of energy hn and not $h(n - n_k)$.

Thus Sadler, Bragg & Porter, and Beatty have all made measurements of the energy of corpuscular radiation emitted from metal plates. Unfortunately the results are very far from consistent, except in so far as they indicate the large effects produced by rapidly moving electrons even when n is only slightly greater than n_k . All three have expressed the energy (more precisely the total ionizing-power) of the electrons emerging from a plate exposed to a primary beam of X-rays, in terms of the energy of the electrons emitted by a layer of air 1 cm. in thickness when traversed by the same primary beam. Let this be R_1 when from the face of incidence, R_2 when from the face of emergence, and let $R = R_1 + R_2$.

We, however, wish to know the relative energies of the corpuscular radiations from layers of metal and air which produce the same absorption of the primary beam. In other words, we wish to know the fraction of the energy of the primary beam which is transformed into corpuscular radiation in the metal plate, as shown by what emerges from its surface. If the corpuscular radiation proceeded in a direction normal to the surface and were absorbed

exponentially with the distance as given by $I = I_0 e^{-\mu x}$, μ having the value μ_a' in air, μ_r' in the radiating plate, then it is quite easily seen that

$$R_{\mu_r'} = \frac{\text{energy corpuscular radiation from metal (thin sheet)}}{\text{energy corp. radiation from air of equal thickness}},$$

and

$$R_{\mu_a'} = \frac{\text{energy corp. radiation emerging from thick metal plate}}{\text{energy corp. radiation emerging from a thick air plate}}$$

$$= \frac{\text{energy of corp. radiation emitted by metal}}{\text{energy of corp. radiation from equal mass of air}}$$

if the absorption of corpuscular radiation is proportional to the density of the absorbing substance.

Dividing the above by the ratio of the mass absorption coefficients of the primary X-radiation in metal and in air, we get the fraction

$$\frac{\text{energy corpuscular radiation from metal}}{\text{energy corpuscular radiation from air}}$$

for equal absorptions of primary beam. But the corpuscular radiation from air is a measure of the energy of the X-radiation absorbed in it*.

Now

$$\frac{\mu_r}{\rho_r} = \text{mass absorption coefficient of primary X-radiation in the metal ;}$$

also

$$\frac{\mu_a - \sigma_a}{\rho_a} = \text{mass absorption coefficient of primary X-radiation in air, after subtraction of the scattering coefficient } \frac{\sigma_a}{\rho_a}.$$

Thus

$$R_{\mu_a'} \div \frac{\mu_r / \rho_r}{\mu_a - \sigma_a / \rho_a} = \text{fraction of energy of primary radiation transformed into energy of corpuscular radiation in the metal,}$$

$$= \frac{k_r'}{\mu_r} \text{ say,}$$

where k' is the coefficient of transformation of the primary X-radiation into corpuscular radiation in the metal.

We can thus determine the fraction of the energy of a primary beam appearing as corpuscular radiation, assuming that what emerges from the surface of the metal is a fair sample of the whole corpuscular radiation. Most of the

* n being much greater than n_k for air.

measurements were made on the radiation from one face alone, Sadler's and Bragg & Porter's from the face of incidence, Beatty's from the face of emergence; we have therefore as an approximation taken R as $2R_1$ or $2R_2$ as the case may be.

Regarding the assumptions, though the corpuscular radiation as measured (*i. e.* that emerging) consisted of rays covering the whole range of velocities from the maximum downwards, and these moved in all directions, the diminution of ionizing power was found by experiments (Sadler) to be connected with the thickness of the absorbing sheet approximately by an exponential law; also the proportionality of absorption with density of the absorbing substance seems to hold at least approximately, in such cases as those to which we wish to apply it. Table IV. gives the determinations on these assumptions from the results of Sadler, Bragg & Porter in curved brackets, Beatty in square brackets.

Beatty's results (for Ag and Se) are the most regular and definite. They indicate at once that when n is less than n_k , practically the whole of the absorption was accounted for by the corpuscular radiation as measured from the Ag plate; but when n was greater than n_k , the corpuscular radiation possessed a fraction increasing from about $1/2$ to the full energy of the absorbed primary radiation. These results agree almost perfectly with the conclusions from the ionization experiments, and find further support from the measurements of the energy of the characteristic radiation. These results seem to justify the calculation based on the plate experiments. They indicate that the corpuscular radiation such as emerges from the surface of a plate gives us a measure of the whole corpuscular radiation as detected in a gas.

There is no indication of the *large* diminution in the value $\frac{k'}{\mu}$ which would have occurred when n slightly exceeds n_k if the K electrons had been ejected with energy much less than hn .

The results of Bragg & Porter (curved brackets), though not so regular, indicate the same thing. The values approximate to unity when n is less than or much greater than n_k , but when n is slightly greater than n_k (see columns for Fe, Ni, Cu, and Zn) somewhat smaller values are recorded. Yet the K absorption in these cases is

* Using Sadler's values of the absorption coefficients for corpuscular radiations.

TABLE IV.

Showing approximate fractions $\left(\frac{k'}{\mu}\right)$ of X-ray energy transformed into corpuscular radiation—as measured from metal plates. From Sadler, Bragg & Porter (curved brackets), Beatty [square brackets].

Radiation.	Al.	Fe.	Ni.	Cu.	Zn.	Se.	Ag.	Sn.
Fe	·106	very small.	very small.	·276 [1·03]	
Co	·128	"	"	·32	
Ni	·66	"	·364	
Cu	·6	·2	·42 [·96]	
Zn	·22 (·74)	·58 (·72)	(·72)	·52 (1·84)	(1·06)	·50 [1·0]	(·82)
As	·365 (1·16)	·50 (·74)	(·70)	·66 (·84)	(·78)	·74 [1·06]	(1·02)
Se	·430	·44	·450	·8	
Sr	·794	·36	·36	[·64]	·98	
Mo	1·2	·26	·22	[·69]	·84	
Rh	1·38	·72	
Ag	1·42	·24	·24	[·76]	·62	
Sn	1·62 (1·10)	·22 (1·10)	(·98)	·18 (·96)	(·94)	[·80]	·50 [·44]	(1·96)
I	[·98]

almost the total absorption, which indicates that the K absorption is attended by an intense K emission from the plates. The energy of the fluorescent characteristic radiation would approximately account for the deficiency. Two values for Zn radiation on Cu and Sn radiation on Sn are evidently very high.

Sadler's results show remarkable variation from Beatty's and Bragg & Porter's. With increasing frequency of primary radiation, the value of $\frac{k'}{\mu}$ in Al rises steadily from a small value to too large a value; in Ag it rises and falls again; in Fe and Cu it commences with negligible values, suddenly and enormously rises, when n exceeds n_k , and subsequently falls away gradually with further increase of n . Though these results differ so markedly from Bragg's and from Beatty's, they indicate quite as pronouncedly that the result of the K absorption is the emission of an intense stream of electrons with energy approximately hn . Shearer's recent experiments, on the other hand, indicate little if any connexion between the electronic emission and characteristic radiations.

More recently, M. de Broglie (and Whiddington) have shown that groups of electrons ejected have energy given by $\frac{1}{2}mv^2 = hn - hn_k$. Unfortunately we do not yet know what fraction these are of the whole number of electrons ejected, or of the number of "K" electrons. In fact the method employed does not distinguish between the various groups of electrons except by their velocity.

Tentatively one of us suggested* that the electrons with energy $hn - hn_k$ were those ejected from the atom with energy hn which subsequently lost energy hn_k in passing through another atom, exciting in it the characteristic radiation of frequency n_k †. Such electrons would probably only form a small fraction of the whole number, and it seems very questionable whether they could produce such well-marked lines as those shown in the beautiful photographs obtained by M. de Broglie.

Our Plate Experiments.

The matter is of such importance theoretically, and the few results obtained by other experimenters on metal plates have been so remarkably inconsistent, that we determined to

* Solvay Conference, Brussels 1921.

† Or it might be ejected with energy hn from a certain system within the atom subsequently losing hn_k in another part of the same atom.

examine the emission of electrons from plates exposed to characteristic radiations of various frequencies including that of the characteristic radiations excited in the substance experimented upon, studying especially *the change* in the emergent corpuscular radiation as the frequency of the primary beam is increased from a value less to one greater than the critical absorption frequency for the plate. For when n is only slightly greater than n_k , the value of $h(n - n_k)$ is very small, so that the energy of ejection from the atom is presumably small. The effect of this is that very few such electrons can possibly emerge from the plate experimented upon. Thus, supposing n to be slightly greater than n_k , if the energy of emission of K electrons is given by $h(n - n_k)$

each K electron has only the fraction $\frac{n - n_k}{n - n_l, n_m, \text{ or } n_n}$
 $= \frac{n - n_k}{n}$ approximately of the energy of the other L, M, N electrons. But more than that, these K electrons can only emerge from a very thin layer of the order $\left(\frac{n - n_k}{n}\right)^2$ of the thickness of that from which the L, M electrons emerge. Thus the K electrons can only produce outside the plate an effect $\left(\frac{n - n_k}{n}\right)^3$ of that of an equal number of the other L, M, N electrons.

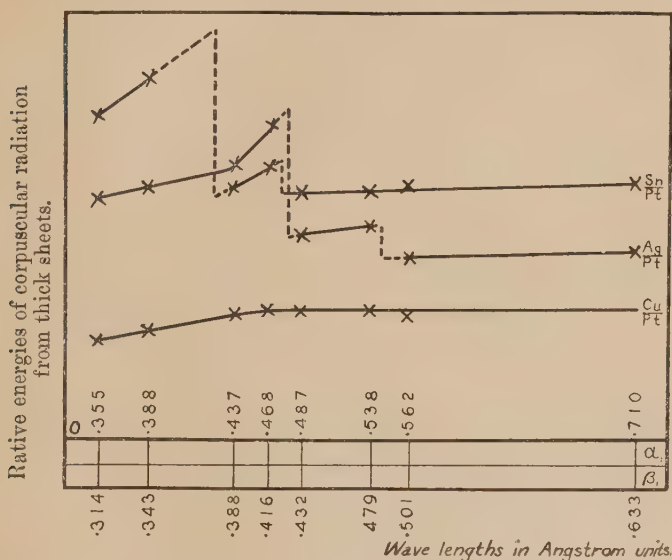
The effect of the K electrons would thus be inappreciable outside the plate when n exceeds n_k slightly. It would appear only very gradually as n increased, no increase being appreciable until n exceeded n_k by something of the order of 30 per cent. or 40 per cent. On the other hand, if the energy of the K electrons from the plate is given by hn , then when n passes n_k there is a sudden increase in the corpuscular radiation emerging from the surface, the K electrons producing ionization proportional to their number.

This experiment was performed using characteristic radiations of series K as exciting radiations. The metal plate experimented upon was placed at the end of an ionization chamber 10 cm. in length containing hydrogen. The front window was of aluminium faced internally with filter-paper. Thus the radiation passed through filter-paper, through the hydrogen, and on to the back plate. The direct ionization of hydrogen by X-rays was negligible, so that the whole ionization observed was that due to electrons from the two faces by which the beam entered and left the

chamber. The emission from the front face when this was of paper was also small, as was seen by performing the experiment with paper faces both front and back. Thus the ionization observed was that produced by electrons from the metal surface at the end of the ionization chamber. A standard for comparison had of course to be employed: this was obtained by using a metal, usually platinum, which has no characteristic radiation within the range of frequencies covered by primary radiations.

The results typical of those obtained from a large number of experiments of this kind are shown in fig. 1, in which the

Fig. 1.



energy of the emergent corpuscular radiation compared with that obtained under similar conditions from platinum is plotted against wave-length of the exciting radiation. It should be remembered that each radiation used in these experiments was a complex radiation, but may be regarded as consisting of only two distinct components, known as the K_α and K_β radiations— K_β the radiation of higher frequency having an intensity about one-fourth that of the K_α radiation. In the figure, the wave-lengths of both the α and β constituents are shown along the horizontal axis, the α constituent being exactly to scale, the β only approximately so, as there is a slight deviation from proportionality of the two. In proceeding from longer to

shorter wave-lengths, the K_β radiation is the first to pass the critical absorption wave-length in the substance experimented upon.

The principal features of interest in the curves are the following :—

Copper.—The corpuscular emission from copper varies little from proportionality with that from platinum. This is as it should be, as there is no spectral line of either within the range covered by these experiments. Even the small gradual diminution of the ratio with increasing frequency at the higher frequency end, would need confirmation. More direct experiments did not show such a variation : we shall return to this again.

Silver.—In the curve for silver, passing from longer to shorter waves two distinct rises occur due to the effects of the two components of the K radiation, in each case when the effective component passes through the critical absorption wave-length, which is somewhat shorter than that of the K_β line for silver.

The relative magnitudes of these increases are, as nearly as can be observed, in the same ratio as the relative intensities of the two constituents themselves.

The total increase in the energy of corpuscular radiation when both constituents pass the critical frequency is about 100 per cent., the rise actually observed with Sb radiation being about 85 per cent. In the case considered, if the energy of the K electrons were given by the relation $\frac{1}{2}mv^2 = h(n - n_k)$ and if all the additional energy absorbed—the K absorption—were transformed into this radiation, the increase observed would be only of the order of 3 per cent.

It must be remembered, however, that the characteristic radiation excited in the plate must itself give rise to a corpuscular radiation when absorbed in its own substance. Thus for instance, when Sb radiation falls on Ag and causes it to emit Ag X-rays (of series K), these Ag X-rays themselves produce an emission of electrons which on either theory possess energy differing little from hn . Calculation (see below *) shows that this would account for a rise of

* Thus the intensity of the exciting primary beam at a depth x is given by $I = I_0 e^{-\mu_1 x}$. This excites characteristic X-radiation, the rate of emission of energy from a thin slab of unit area and thickness δx being $kI_0 e^{-\mu_1 x} \delta x$, where k is the transformation coefficient.

The energy of the characteristic radiation passing out through the surface in a direction between the angles θ and $\theta + \delta\theta$

$$= \frac{2\pi \sin \theta \cdot \delta\theta}{4\pi} kI_0 e^{-\mu_1 x} \delta x (e^{-\mu_2 x \sec \theta}) \times k_2' t_2 \sec \theta,$$

where k_2' is the coefficient of transformation of characteristic X-radiation

something like 35 per cent. in the corpuscular emission from the silver plate, leaving say a 50 per cent. rise due to the more direct action of the primary X-rays. The order of magnitude of this secondary effect is, however, too close to that measured to enable us to arrive at confident conclusions without further evidence. In order more directly to test this point, we made experiments on very thin sheets (thickness .0003 cm.) from which the secondary effect of the fluorescent radiation was only about $\frac{1}{3}$ of that from the thick sheet; consequently the corpuscular emission due to this was reduced by $\frac{2}{3}$. The difference between the effects from thick and thin sheets was experimentally found to be quite appreciable (see fig. 2), the increase for the thin sheet being diminished to about 60 per cent. From these results again it might be concluded that the effect produced by the more direct action of the primary rays—that is, the sudden increase occurring in the ionization produced outside the silver plate, caused by electrons ejected under the direct influence of the primary radiation when

into corpuscular radiation, and t_2 is the effective thickness of the surface layer contributing to the corpuscular radiation emerging.

The energy of corpuscular radiation emitted per sec. from the surface and due to the secondary characteristic radiation proceeding in direction between θ and $(\theta + \delta\theta)$

$$= \frac{1}{2} k k_2' t_2 I_0 \tan \theta \delta\theta \int_0^d e^{-(\mu_1 + \mu_2 \sec \theta)x} dx,$$

where d is the thickness of the plate,

$$= \frac{1}{2} \frac{k k_2' t_2 \tan \theta}{\mu_1 + \mu_2 \sec \theta} I_0 \{ 1 - e^{-(\mu_1 + \mu_2 \sec \theta)d} \} \delta\theta.$$

\therefore Total energy emission per sec. in corpuscular radiation due to the secondary characteristic X-radiation

$$= \frac{1}{2} k k_2' t_2 I_0 \int_0^{\pi/2} \frac{\sin \theta}{\mu_1 \cos \theta + \mu_2} \{ 1 - e^{-(\mu_1 + \mu_2 \sec \theta)d} \} d\theta.$$

The corpuscular emission due to the direct action of the primary X-radiation is $k_1' t_1 I_0$, where k_1' is the coefficient of transformation of the primary into corpuscular radiation, and t_1 is the effective thickness of the layer contributing to the surface emission.

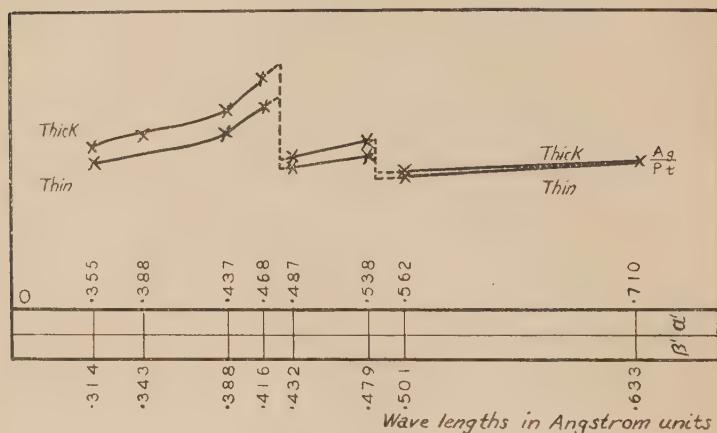
Now the only assumption we need make in order to obtain a fairly accurate measure of the effect of the corpuscular radiation excited by the secondary characteristic X-radiation, is that the fraction of the energy of corpuscular radiation emerging through the surface from the very thin effective layer is the same when the exciting X-radiation spreads in all directions as when it passes through the thin sheet normal to the surface,—that is, of course, for equal absorptions of energy in the thin sheet.

All the evidence points to the conclusion that for a given absorption of energy of a definite X-radiation in the surface layer, the difference between the two would be small.

Assuming exact equality then, if there were no true K corpuscular

its frequency slightly exceeded its critical value—was not more than about 50 per cent. Ionization-pressure curves were obtained to test if the increase were due to swiftly-

Fig. 2.



moving electrons. These left no doubt that the additional ionization was due neither to a soft X-radiation nor to a corpuscular radiation of slowly-moving electrons. Energy considerations alone show the latter to be impossible except by a release of atomic energy, as the intensity would need to be enormous to produce the observed effects from the

emission, that is, if all the observed rise were due to the secondary characteristic radiation,

and $\frac{k_2'}{k_1}$ would $= \frac{\mu_2}{\mu_1} = \frac{\lambda_2^3}{\lambda_1^3}$ fairly accurately,

$$\frac{t_2}{t_1} = \frac{\lambda_1^2}{\lambda_2^2},$$

from Whiddington's Absorption Law for rapidly moving electrons and the Planck-Einstein relation $\frac{1}{2}mv^2 = hn$.

Thus the ratio $\frac{\text{secondary characteristic radiation effect}}{\text{primary radiation effect}}$ would be

$$\frac{1}{2}k \frac{\lambda_2}{\lambda_1} \int_0^{\pi/2} \frac{\sin \theta}{\mu_1 \cos \theta + \mu_2} \{1 - e^{-(\mu_1 + \mu_2 \sec \theta) d}\} d\theta.$$

The coefficients of absorption μ_1 and μ_2 of the primary and secondary radiations in silver are known accurately; the wave-lengths of these K radiations are also known; k is known for the transformation of radiations into characteristic radiations in various metals, and in the case of Sb radiation of K series in Ag is about .4. Hence the above fraction may be calculated.

exceedingly thin layer of metal which would be effective. The same argument would apply to very soft characteristic radiations such as would be completely absorbed in 10 cm. of hydrogen.

Thus the sudden rise in the corpuscular radiation from silver when the exciting radiation is of slightly higher frequency than the K_β radiation of silver, is very much smaller than might have been expected from the results obtained from previous experiments, but again such effect as there is cannot be explained by the emission of electrons with energy $h(n - n_k)$.

Tin.—The curve showing the corpuscular emission from Sn relative to that from Pt is similar to that from Ag, the discontinuities occurring at a higher frequency corresponding to the higher critical absorption frequency.

These results, then, only partially support our previous conclusion drawn from the results published by other observers. They indicate that some electrons emitted in association with the K fluorescent radiation possess the full energy hn , or at any rate a value very near to this. But it appears from these experiments that this radiation does not account for anything like the whole of the additional energy absorbed, for the increase in absorption is something of the order 700 per cent. Thus the fraction of this energy absorbed—the K absorption—appearing in the rapidly moving corpuscles when n is slightly greater than n_k is only of the order of 7 per cent. instead of a possible 50 to 60 per cent. (The energy of the characteristic X-radiation emitted appears by extrapolation from Sadler's results to be of the order of 40 per cent. of the K absorption.)

The difference between 7 per cent. and a possible 60 per cent. for the corpuscular radiation (or nearly 50 per cent. actually observed by the ionization method in (C_2H_5Br) suggests the possibility of an emission of other electrons with energy considerably less than hn , as those observed by de Broglie. These would not escape from plates in sufficient number to produce an appreciable ionization outside, but in gases they would produce an ionization proportional to their energy.

It is difficult to reconcile our results with the results of measurements of Sadler, of W. H. Bragg, and of Beatty, which all led to the conclusion that approximately all the electronic emission was in the form of electrons with energy hn . These experiments have, however, been made

upon other elements. The investigations are being continued, but the discrepancies suggest the influence of factors not hitherto taken into consideration.

Again, the corpuscular emission as observed from Ag and Sn plates (compared with the standard Pt) appears to fall off again to a certain extent as n increases beyond the critical value n_k , and when n is considerably greater than n_k the corpuscular emission becomes very small. This is not what we expected, for it accentuates the discrepancy between energy absorbed and that re-emitted in the form of the rapidly moving electrons. There is, however, agreement in this respect with the results obtained by Sadler for Fe and Cu. It might of course be accounted for by a possible selective absorption of electrons moving with energy greater than hn_k in an element with characteristic frequency n_k , but this effect is probably very small.

It appears, therefore, that the electronic emission which we have been studying is most intense when the frequency of the primary X-radiation is very near to the critical absorption frequency.

SUMMARY.

The energy of the corpuscular radiation emitted by metal plates when exposed to X-radiation of varying frequency has been investigated by a simple method (previously used by one of the authors in a few isolated cases). The results differ substantially from those obtained by other investigators by different methods.

They show two independent discontinuities in corpuscular emission due to α and β constituents of the K radiation when this was used to excite corpuscular emission.

They show that few K electrons, *i. e.* those electrons emitted in exclusive association with the K characteristic radiation whatever their origin, have energy of the order hn , where n is the frequency of the exciting radiation.

From silver and tin, these electrons (unless their full energy is concealed by a selective absorption of improbable magnitude in the substance emitting them) are altogether insufficient in number to account either for the observed increase in ionization, *i. e.* for the whole K ionization when the substance is in the gaseous form, or for the full energy of characteristic radiation on the basis of one quantum of characteristic radiation for one high-speed electron.

In this respect these results differ most markedly from

those obtained by previous experimenters on the emission from metal plates.

The inadequacy of these electrons thus points to the importance of the part being played by other electrons with energy $h(n-n_k)$, such as found by de Broglie; these would not be detected by the plate experiments.

On the other hand, the ionization experiments of Barkla and the results of experiments by Sadler, by Beatty, and Bragg, on the emission of electrons from metal plates, all indicate that the bulk of the energy in the corpuscular radiation—the K corpuscular radiation—is in electrons of energy approximately hn . Such experiments have been made, however, in substances of lower atomic weights. These substances are now being studied by more exact methods.

II. *An Experimental Determination of the Rate of Decay of the Short-Life Product Radium C'. By J. O. JACOBSEN, Physicist at the Medical Radium Institute, Copenhagen*.*

IN 1911 Geiger and Nuttall† found a simple relation between the transformation constant λ for radioactive substances emitting α -rays and the range R of the α -rays, namely, that the points obtained by plotting $\log \lambda$ against $\log R$ are situated nearly on a straight line, or

$$\log \lambda = a + b \log R,$$

where the constant a has somewhat different values for the three radioactive families. More accurate measurements carried out later by Geiger‡ show that the formula is not exact, as within each of the radioactive families deviations are found which can hardly be explained by errors of measurement. The agreement between the formula and the measurement is best for the Uranium-Radium family, where, among the substances for which both λ and R are known with some accuracy, only the emanation with certainty falls outside the curve.

The best agreement with the experiments is obtained with the following values of the constants:

$$a = -41.0, \quad b = 59.3.$$

* Communicated by Prof. Sir E. Rutherford, F.R.S.

† Phil. Mag. xxii. p. 613 (1911).

‡ Zs. für. Phys. viii. p. 45 (1921-22).

The range of the α -rays from RaC' is 6.608 cm. ; with the above values of a and b this gives for the transformation constant

$$\log \lambda = 7.7, \quad \lambda = 5 \cdot 10^7 \text{ sec.}^{-1},$$

or the half-period value $T = 0.35 \cdot 10^{-7} \text{ sec.}$ The decay of a substance like this cannot of course be examined by ordinary experimental means; in fact, if one could prepare pure RaC' , the substance would practically have disappeared 10^{-6} sec. after the preparation. On the other hand, the peculiar character of the formula and the fact that no successful theoretical explanation has hitherto been given, invite further experimental investigation. If a direct measurement of the transformation constant λ for RaC' could be carried out, the values of λ for which the validity of the formula could be tested would be extended from 10^{-18} to 10^7 , the value of λ deduced from the formula supposed to be correct.

Experimental Method.

The value of λ is (supposedly) of the order of magnitude 10^7 sec.^{-1} . In seeking for a suitable method to measure λ the problem is to find a known quantity of the same order of magnitude, with which λ can be compared. The most suitable quantity for this purpose seems to be the velocity of the recoil atoms from RaC . If M and V denote mass and velocity of the recoil atom, V is calculated from

$$\frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \cdot v = M \cdot V,$$

where m_0 is the mass and v the velocity of the β -particle. In the calculation of V the difficulty at once appears that the β -rays from RaC are complex, so that the value of v to be introduced cannot be fixed. Without entering into a detailed discussion of the origin of the β -rays, we may suppose that the primary β -rays from a definite radioactive substance all have the same velocity, so that at least part of the β -rays from RaC are secondary. Further, we may suppose that the primary β -rays have a higher velocity than the secondary ones, so that the value of v to be introduced into the formula is to be chosen from among the highest values found for the velocities of the β -rays. The highest

value which has been measured seems to be $v=0.996.c.*$. From this value we obtain

$$V=8.4 \cdot 10^5 \text{ cm./sec.}$$

Too much stress should not be laid on this special value for V , as it is chosen somewhat at random, but for the present it may be used to illustrate the experimental method.

Consider a plate covered with RaC' . From the plate a stream of atoms of RaC' will be sent out moving with a velocity of $8.4 \cdot 10^5 \text{ cm./sec.}$ When such a recoil atom has moved a certain distance, it is transformed into an atom of RaD with the emission of an α -particle, which may be detected on a zinc-sulphide screen. By measuring the diminution of the number of RaC' atoms with increasing distance from the plate, the transformation constant λ of RaC' may be determined from the velocity V of the recoil atoms or *vice versa*.

For the decay of RaC' we have

$$n=n_0 \cdot e^{-\lambda t},$$

where λ from the Geiger-Nuttall formula is calculated to be $3.2 \cdot 10^7$. By introducing $t=\frac{\chi}{V}$, where χ is the distance from the active plate and V the velocity of the recoil atoms, we get

$$\log_e \left(\frac{n_0}{n} \right) = \frac{\lambda}{V} \cdot \chi.$$

As the number of α -particles emitted is proportional to the number of atoms present, n may denote the number of scintillations per minute on a suitably placed zinc-sulphide screen; thus, by plotting the logarithm of the number of scintillations against the distance from the active plate, the curve should be a straight line, whose slope determines $\frac{\lambda}{V}$.

The Experiments.

When carrying out the experiments screens must be placed in a suitable way, so as to obtain firstly an approximately parallel beam of recoil atoms, and secondly so that the α -particles observed are emitted in a direction perpendicular to that of the recoil atoms. After some trials to find

* Danysz, *Le Radium*, iii. p. 949 (1913); Rutherford, *Phil. Mag.* xvi. p. 717 (1913).

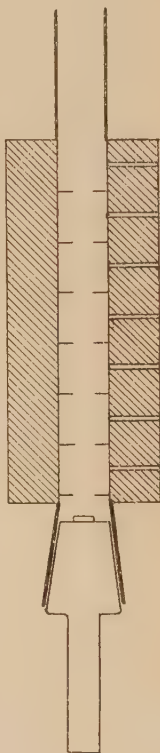
26 Mr. J. C. Jacobsen : *Experimental Determination of the*
suitable dimensions of the apparatus, the following form was
chosen :—

The apparatus consisted of a brass tube of square cross-section and 10 mm. internal diameter (fig. 1), the thickness of the walls being about 10 mm. In one side of the tube a number of slits 1 mm. in width were cut 6 mm. from one another. The extension of the slits perpendicular to the paper was 10 mm. The slits were closed by a mica leaf with 3.5 cm. air equivalent, fastened with sealing-wax on the outer side of the tube. Half way between the slits a number of screens with square openings 4×4 mm. were placed to prevent reflexion from the walls of α -particles coming from the active source. This was a nickel plate, which was placed in a cone in the lower end of the apparatus. The other end of the brass tube was connected to the pump, McLeod manometer, and an arrangement for letting in small quantities of air. Mercury vapours were kept away from the apparatus by a U-tube immersed in liquid air. The zinc-sulphide screen was attached to a microscope which could be moved in vertical direction.

As radioactive material it is necessary to use pure RaC (not active deposit). The active deposit on a metal plate is not situated solely on the surface, but, on account of the recoil from RaA, the RaB (and RaC) atoms are spread uniformly over a layer whose thickness is the range in the metal of the recoil atoms from RaA (of the order of magnitude 10^{-5} mm.). This is of no importance when working with α -rays, but in these experiments it is essential that the active material should be situated on the surface of the metal on account of the smallness of the energy of the β -rays; in fact, when using active deposit, the RaC' atoms would have all velocities from zero to a maximum value.

RaC was prepared in the following way :—About 100 millicuries of emanation were collected in a glass tube over mercury and left there for 3–4 hours. The emanation was then pumped off, and the active deposit dissolved in 1–2 c.c. of diluted hydrochloric acid. When placing a polished nickel disk in the hot solution for some minutes, RaC' is obtained on the disk. To obtain pure RaC it is necessary to

Fig. 1.



wait until RaA has decayed. To avoid radioactive contamination the glass tube was heated with a Bunsen burner while the emanation was pumped off, and the nickel disk after activation was washed in distilled water and alcohol, and afterwards heated for a few minutes in a vacuum. The metal is attacked somewhat by the acid, though not much, and a polished plate as a rule keeps completely bright; only in a few cases was the plate slightly stained. In this way deposits with a γ -activity of about 5 mgrs. could be obtained. When the plate had been prepared, it was placed in the cone and the pump set in action. After 5 minutes pumping the pressure as a rule was lower than 0.0001 mm., and the measurements could be commenced. The microscope, with the zinc-sulphide screen, was placed in front of one of the slits, where the number of scintillations had a suitable value (as a rule No. 3 or 4 from below). The number of scintillations was counted, the time for each measurement being noted. When a suitable number of α -particles (100-400) had been counted, the microscope was moved downwards to the next slit, and the measurement repeated, etc.

The results now have to be corrected for the decay of the active source and for the fact that the solid angle, over which the beam of recoil atoms extends, changes when moving from one slit to another. As already mentioned, the screens all had the same aperture, 4×4 mm., so that the solid angle over which the beam of recoil atoms extends is inversely proportional to the square of the distance from the source to the corresponding screen. The following figures, which are taken from an actual experiment, may serve as an illustration:—

Slit No.	d_1 .	d_2 .	N_0 .	n .
4	25 mm.	21.8 mm.	13	6.2
3	19 „	15.8 „
2	13 „	9.8 „	195	18.7
1	7 „	3.8 „	1800	26.0

d_1 is the distance from the source to the slits, d_2 the distance from the source to the corresponding screens, N_0 is the number of scintillations in 100 seconds corrected for the decay of the source, under n is quoted $10^{-3} \cdot N_0 \cdot d_2^2$, n thus being proportional to the number of atoms transformed per unit time. If $\log_e n$ is plotted against d_1 , an approximately straight line is obtained, the slope of which is 0.81. The result of this experiment thus is $\frac{\lambda}{V} = 0.81$.

The question now arises whether the scintillations observed

are really due to α -particles being expelled from recoil atoms, and are not for instance due to α -particles coming from the active source and deflected by the walls and the edges of the screens. It is, however, very easy to make a control experiment on this point by letting a small quantity of air into the apparatus. On account of their small energy the recoil atoms will be stopped at a short distance from the source, at a pressure at which the α -particles will not suffer any sensible decrease of velocity. The number of α -particles counted usually was 10-60 per minute. By letting air into the apparatus to a pressure of about 1 mm. of mercury, the number of scintillations went down to 1-5 per minute, and when the air was pumped out, the number of scintillations went up to the former value.

The experiments hitherto performed have given values for $\frac{\lambda}{V}$ lying between 0.8 and 1.2 with a mean value of $\frac{\lambda}{V} = 1.0$. On account of extraneous circumstances the experiments must be postponed for some time, the uncertainty of the result thus being rather great. As will appear from the sequel, this, however, is not essential for the discussion of the result.

If in $\frac{\lambda}{V} = 1.0$ we put $V = 8.4 \cdot 10^5$ (corresponding to a velocity of 0.996 of the β -rays), as result of the measurements is obtained

$$\lambda = 8.4 \cdot 10^5$$

or

$$\log_{10} \lambda = 5.9,$$

while the value predicted by the Geiger-Nuttall formula is

$$\log_{10} \lambda = 7.5.$$

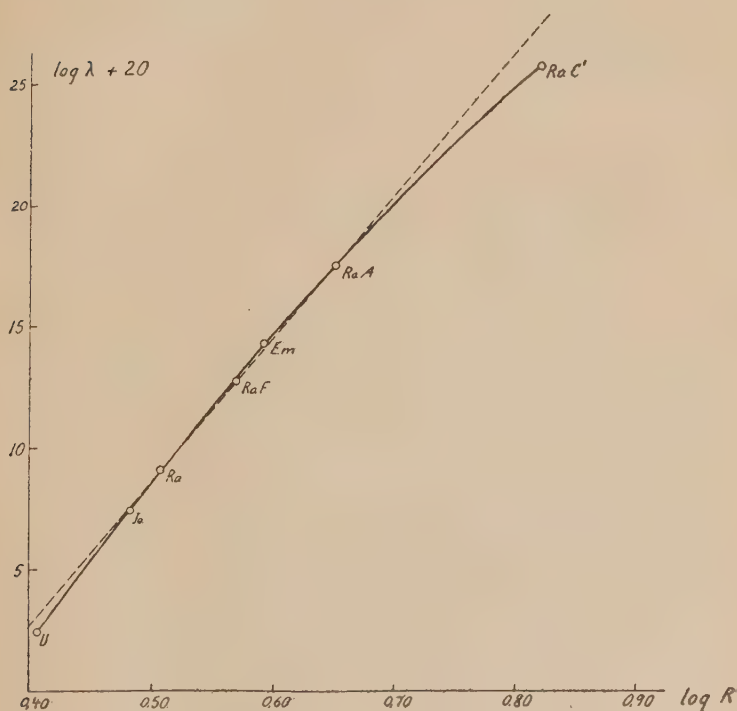
To see if the agreement between these values is satisfactory, consider a little more closely the quantities λ and V . A change in the experimental value for $\frac{\lambda}{V}$ of 100 per cent. would only give a change in $\log \lambda$ of about 6 per cent., thus being of no importance. If V is calculated from $\frac{\lambda}{V} = 1.0$ and $\log_{10} \lambda = 7.7$, we get

$$V = 5 \cdot 10^7,$$

a value which is 60 times greater than $V = 8.4 \cdot 10^5$, which has hitherto been used. Consequently, if the value of λ predicted by the Geiger-Nuttall formula is correct, the

momentum of the primary β -rays from RaC should be 60 times greater than corresponding to $v=0.996c$. Even if it may be considered as questionable whether by the experiments hitherto performed there has been any possibility for measuring so high velocities, because the deflexion of an electrified particle in a magnetic field is inversely proportional to the momentum of the particle, so that very strong magnetic fields would be required, it would certainly appear very improbable that such hard β -rays should be emitted from RaC. From these considerations it appears, therefore, that the value of λ predicted by the Geiger-Nuttall formula is definitely too high.

Fig. 2.



On the other hand, the value of λ calculated by the Geiger-Nuttall formula is not determined very exactly. The fact that the emanation definitely falls outside the curve indicates that the formula is only a first approximation, an assumption which is supported by a closer inspection of the figures. On fig. 2 the values of $\log \lambda$ given by Meyer

and v. Schweidler are plotted against $\log R$ taken from Geiger's paper *. The value of λ for RaC' is the one which is obtained by the present experiments, using $V = 8.4 \cdot 10^5$ for the velocity of the recoil atoms. The straight line (dotted) represents the Geiger-Nuttall formula. It is at once obvious that a slightly curved line gives a better agreement with the experimental values. By these considerations we are led to the assumption that the function $\lambda = f(R)$ in reality is represented by some slightly curved line, although the experiments yet are not sufficiently exact to settle this point definitely.

For the corresponding product of the Thorium sequence ThC' , the value of λ predicted by the Geiger-Nuttall formula is about $10^{-11} \text{ sec}^{-1}$. If this value is of the right order of magnitude, it seems impossible to obtain a comparison with the velocity of the recoil atoms from ThC , because the proportion $\frac{\lambda}{V}$ will differ widely from unity, since V certainly cannot be much more than 10^6 . However, the experiment ought to be performed, but at present sufficiently strong Mesothorium preparations are not at the author's disposal.

Control Experiments.

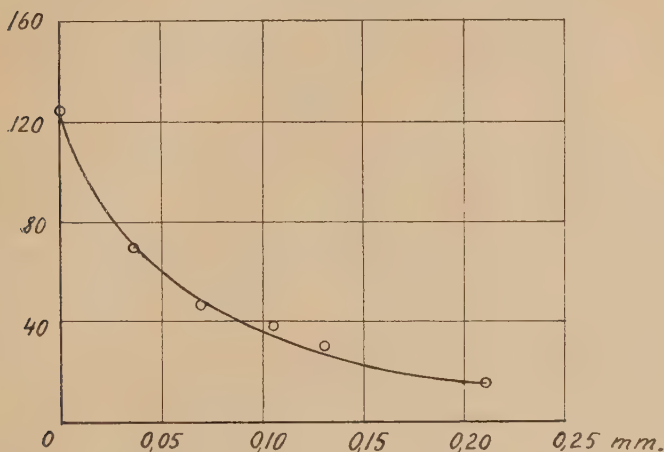
The reliability of the results would be increased if the velocity of the recoil atoms could be determined without knowing the velocity of the β -rays. This may be done either by determining the deflexion of the recoil atoms in a magnetic field or by measuring the range in air. The first possibility involves the difficulty that it is unknown whether the recoil atoms from RaC in a vacuum possess an electric charge, and, in addition, very strong magnetic fields would be required. If the recoil atoms have a single electric charge, they will suffer the same deflexion as the corresponding β -rays, but owing to the rapid diminution of the number of recoil atoms with increasing distance from the source, it is necessary to use circles with a small radius. A determination of the range is more easily carried out, but requires a calculation of the connexion between range and velocity. [Experiments to determine the range in air are in progress.]

Although the experiments at this point are rather

* Geiger, *l. c.*

incomplete, a preliminary result may be given here (fig. 3). The microscope was set at a fixed distance (12.7 mm.) from the source, and the scintillations counted with air at different pressures in the apparatus; intermediate countings in vacuum were taken for control, showing that the decay of the source took place according to a half-value period of 19.5 minutes.

Fig. 3.



In fig. 3 the number of scintillations in 100 seconds, corrected for the decay of the source, are plotted against the pressure (in mm. Hg) in the apparatus. The number of scintillations falls off approximately exponentially with increasing pressure.

Summary.

1. RaC' has been observed in an isolated state, the emission of α -particles having been observed under such circumstances that the α -particles cannot be due to any other substance.

2. For the transformation constant λ of RaC' is found

$$\log_{10} \lambda = 5.9,$$

a value which, by a comparison with the other products of the Uranium-Radium sequence, suggests a modification of the Geiger-Nuttall formula.

The experiments were carried out at the Institute of Theoretical Physics with material from the Medical Radium Institute. The author wishes to express his thanks to the Managing Board and to Professor Bohr for the facilities afforded.

III. *A Determination of the Vapour Pressures of Cæsium and Rubidium, and a Calculation of their Chemical Constants.* By D. H. SCOTT, *D.Phil.**

THIS paper describes the determination of the vapour pressures of Cæsium and Rubidium between 50° C. and 130° C. with the aid of a vibrating quartz fibre manometer. From the figures obtained the chemical constants of the two metals were calculated and found to be in agreement within the experimental error with the formula

$$C = 1.5 \log M + C_0$$

(where C is the chemical constant, M the molecular weight, and C_0 the "absolute chemical constant"). The work was undertaken not so much with the object of verifying this formula—which may fairly be regarded as established—as in the hope of supplying further information about the vapour pressures of monovalent elements, which may be of value in future work on the nature of the inter-atomic forces.

The original quartz fibre manometer described by Haber (*Zeitschrift für Elektrochemie*, xx. p. 296 (1914)) consists essentially of a quartz fibre about .4 mm. thick and 9 cm. long, supported inside a wide glass tube. The fibre is observed through a microscope and illuminated from the side. When the fibre is at rest a sharp line of light is seen in the field of view, and if the fibre is set in vibration this line broadens out into a band whose width can be measured on a scale in the eyepiece of the microscope. The method of using the instrument consists in observing the time taken for the amplitude of vibration to diminish to a definite fraction of its original value. This time T is connected with the pressure by the relation

$$b = T(\Sigma p M^{1/2} + a), \quad (1)$$

where a and b are constants determined by calibration against a McLeod gauge. The term $\Sigma p M^{1/2}$ is formed by adding together the products of the partial pressures of the various gases present and the square roots of their respective molecular weights. In Haber's original gauge the fibre was set vibrating by tapping the instrument with the finger. This method did not prove at all satisfactory, as it was found extremely difficult to produce vibrations in a plane. As a rule a compound vibration was set up which made the edges

* Communicated by Prof. F. A. Lindemann, F.R.S.

of the observed band of light oscillate to and fro in such a way that accurate reading was impossible. The problem was finally solved by fusing about three turns of very fine iron wire on to the tip of the quartz fibre so that the vibration could be controlled with an electromagnet operated by a tapping key. By this means it was possible to produce vibrations regularly in a plane, so that the edges of the observed band of light were quite sharp and its width could be accurately measured. The extra weight of the iron tip increased considerably the time required for the amplitude to diminish by its definite amount, and in consequence a somewhat thicker quartz fibre was used ($7\text{ mm.} \times 8.3\text{ cm.}$ for the manometer used for the measurements on mercury; $8\text{ mm.} \times 8.9\text{ cm.}$ for that used for the cesium and rubidium).

The fibre was fused directly on to a quartz rod about 6 mm. thick and 6 cm. long. The method of fixing this quartz rod into the outer glass-work will be seen clearly in fig. 1. AB is a glass tube which fits the quartz as closely as possible. It is constricted very slightly at B. The quartz with the fibre attached is introduced from the top and tapped well down. The glass tube is then sealed off at A. This has been found to make a sound mounting and has proved quite satisfactory. The quartz rod was ground flat on two sides so that any gas in the tube above could pass out freely when the apparatus was being exhausted.

Experience has shown that one precaution is necessary with this mounting. Whenever the apparatus is heated to get gas out of the glass the gauge must be turned into a horizontal position. If this is not done, the quartz rod sinks down when the apparatus is hot and cracks the glass near the constriction on cooling.

In practice the time observed was that required for the band of light to diminish in width from 50 scale-divisions (about 0.63 mm.) to 40 scale-divisions, *i.e.* the time required for the amplitude to diminish to $\frac{4}{5}$ of its original value. Three readings at each pressure were taken, and as a rule the difference of the extreme readings was not more than 1.5 per cent.

The manometer was calibrated against a McLeod gauge of the usual pattern, with a multiplication factor of $6.64 \cdot 10^{-5}$. A trap immersed in liquid air prevented any mercury vapour from getting from the McLeod gauge into the manometer, and the total pressure in it was then that given by the McLeod gauge. Readings of the two gauges were taken at various pressures, and from these the constants

a and b in the equation $b = T(\Sigma p M^{1/2} + a)$ were determined. For air $\Sigma p M^{1/2} = 5.38p$, so that the calibration equation is therefore

$$b = T(5.38p + a). \quad . \quad . \quad . \quad . \quad (2)$$

We can calculate the most probable values of a and b in the usual way by solving the normal equations

$$nb = 5.38 \Sigma p_1 T_1 + a \Sigma T_1,$$

$$b \Sigma T_1 = 5.38 \Sigma p_1 T_1^2 + a \Sigma T_1^2,$$

where n is the number of readings.

Table I. shows the calibration readings for the gauge which was actually used in the determination of the vapour pres-

TABLE I.
Calibration Readings.

	T (seconds).	p (mm. of Hg).	$\theta_{\text{Abs.}}$	$\theta'_{\text{Abs.}}$	$p' \left(= p \sqrt{\frac{\theta'}{\theta}} \right)$	$p'_{\text{Calc.}}$
1	507	$< 10^{-5}$	288.6	423.0	$< 10^{-5}$	$5.1 \cdot 10^{-6}$
2	370	$2.48 \cdot 10^{-4}$	288.0	421.3	$3.00 \cdot 10^{-4}$	$3.10 \cdot 10^{-4}$
3	274	5.12	288.0	426.8	6.24	6.38
4	208	8.76	287.8	421.5	$1.06 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$
5	188	$1.01 \cdot 10^{-3}$	288.0	423.6	$1.22 \cdot 10^{-3}$	1.22
6	150	1.39	288.1	425.7	1.69	1.68
7	141	1.52	287.5	424.3	1.84	1.83
8	125	1.77	287.5	423.5	2.15	2.18
9	113	1.71	287.4	422.3	2.08	2.44
10	86	2.81	287.7	421.0	3.40	3.40
11	68.2	3.68	288.0	426.1	4.48	4.41

Readings 1 and 9 not used in the determination of most probable values of a and b .

$$\begin{aligned} b &= T(5.38 p' + a), \\ \text{whence } b &= 1.863, \\ a &= 3.361 \cdot 10^{-3}. \end{aligned}$$

tures of caesium and rubidium. While taking the measurements on caesium and rubidium the fibre manometer had to be kept at a temperature of about 150°C. to prevent any of the metal condensing in it. In order to eliminate any error that might be caused by change of the constants a and b with temperature the gauge was calibrated at 150°C. The air pressure in the gauge was in consequence higher than

that shown by the McLeod. The values given by the McLeod were therefore multiplied by $\sqrt{\frac{\theta'}{\theta}}$ (θ' =temp. of fibre manometer, θ =temp. of rest of apparatus) to give the true pressure inside the fibre manometer.

The last column in Table I. gives the results of re-calculating by equation (2) the pressures corresponding to the values of T given in the first column.

Before proceeding to the measurement of the vapour pressures of caesium and rubidium it was decided to carry out a check determination of the vapour pressure of mercury. If readings of both the gauges are taken when the trap is not in liquid air, the vapour pressure of mercury at room temperature can at once be determined. For the only gases in the apparatus are air and mercury vapour; the fibre manometer gives the total pressure, and the air pressure is given by the McLeod gauge. The fibre manometer actually used in this determination unfortunately cracked during heating preparatory to being used for caesium and rubidium—and it has not been thought worth while to give the calibration readings in full. The values of the constants in equation (1) were $a=2.67(4) \cdot 10^{-3}$ and $b=1.97(0)$. The results obtained are shown in Table II. T is the time in seconds required for the amplitude of vibration of the fibre to diminish from 50 to 40 scale-divisions. p is the air pressure as shown by the McLeod gauge, θ the temperature of the apparatus, and π_θ the vapour pressure of mercury at $\theta^\circ \text{C}$. The last column gives the value of π corrected to 20°C .

The consistency of these results compares favourably with those obtained by Haber (*Zeitschrift für Elektrochemie*, xx. p. 301 (1914)). He gives the value for π_{20} as $1.26 \cdot 10^{-3}$. This is the result of a weighted mean of two series of observations. The first series consists of seven readings giving results varying between .00112 and .00152, the second of four readings giving results between .00105 and .00140.

At the same time the mean value .00130 is rather higher than both Haber's (.00126) and Knudsen's (.00119). Egerton (*Phil. Mag.* xxxix. Jan. 1920), after a careful examination of the experimental evidence, concludes that the true value lies between .00119 and .00126—probably nearer Knudsen's value than Haber's. But it is interesting to note that the most recently published accurate determination of the vapour pressure (Hill, 'Physical Review,' vol. xx. p. 266 (1922)) gives the value of π_{20} as .00182.

TABLE II.
Vapour Pressure of Mercury.

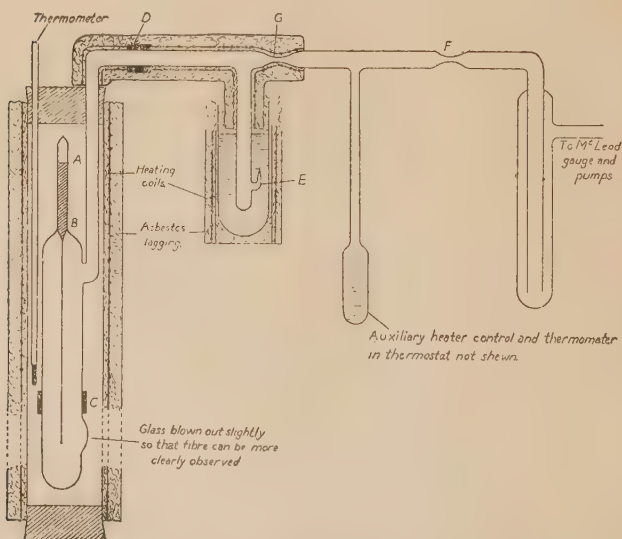
T.	p .	θ° C.	π_{θ} .	$\pi_{20^{\circ}}$.
139	$2.66 \cdot 10^{-3}$	15.0	$8.02 \cdot 10^{-4}$	$1.25 \cdot 10^{-3}$
125	7.30	15.3	8.96	1.36
121	$2.41 \cdot 10^{-4}$	15.4	8.71	1.31
116	5.12	15.1	8.16	1.26
61	$3.22 \cdot 10^{-3}$	15.3	8.69	1.32

Mean $1.30 \cdot 10^{-3}$ mm.

Determination of the Vapour Pressures of Cæsium and Rubidium.

The arrangement of the apparatus was that shown in fig. 1. The fibre manometer was supported by two clamps

Fig. 1.



at C and D attached to a vertical iron support about 2 feet high. This support was rigidly fixed at the bottom to a stone table and at the top by an iron bracket to the wall. The manometer was surrounded by an air-bath consisting of an iron tube 5 cm. in diameter, wrapped with asbestos, and

heated electrically. The bath was kept at a temperature of approximately 150°C. , determined by means of a mercury thermometer graduated in half-degrees. As this tempera-

ture only occurs in the correction formula $p = p' \sqrt{\frac{\theta'}{\theta}}$

a small error in its determination would not be serious.

The metal was contained in the bottom of the branch tube in the middle, connected to the gauge by tubing of .8 cm. internal diameter. This connecting tube was covered with a thin layer of asbestos, wound with nichrome wire and then lagged with more asbestos. By passing a current through the wire the connecting tube was also kept at a temperature of about 150° , so that the tube in the thermostat was the coldest part of the apparatus.

Before the cæsium was distilled into this branch tube and before the charcoal bulb was attached to its side tube, the manometer was calibrated at 150° in this air-bath, and not touched until the conclusion of the experiment. After calibration the charcoal bulb was attached and the cæsium introduced through the side tube (E) by a series of five successive distillations. A small tube containing about .5 c.c. of the metal was cooled in liquid air, the capillary end of it was broken and the tube passed quickly inside a wider tube (also cooled)—connected by a series of bulbs to the branch tube (E). The tube containing the cæsium was sealed up and the apparatus evacuated. With the pumps running the metal was distilled out into the surrounding tube and then slowly from bulb to bulb, in order to get rid of as much of the adsorbed gas as possible. Each distillation occupied about three-quarters of an hour, and each bulb was sealed off and removed as soon as the metal had been expelled from it. There was a slight residue left after the first and second distillations, but none after the subsequent ones. During the process the trap between this part of the apparatus and the McLeod gauge and pumps was kept in liquid air in order to prevent any mercury vapour getting through to the cæsium or rubidium. When the metal had been distilled into the branch tube and the side tube sealed off, the capillary at F was sealed up. The apparatus was left some hours in case the metal gave up any more gas, after which the charcoal bulb was put in liquid air and the capillary at G sealed up. In both cases the capillaries F and G were just closed and not detached in order that the gauge supports might be as nearly identical as possible during the experiment and during the calibration.

In order to determine how much residual gas was left in

the apparatus the branch tube containing the metal was placed in a mixture of CO_2 snow and ether. This reduced the vapour pressure practically to nil, and a reading of the manometer was taken. This was also done at the conclusion of the experiment and the mean value taken as the residual gas pressure during the experiment.

The branch tube was now placed in a thermostat and readings of the gauge taken at various temperatures. It was found impossible to use any thermostat in which a stirrer was employed, as the motion of the fluid affected the vibration of the fibre. In consequence a small mercury thermostat was constructed. A glass tube (4×11 cm.) surrounded by an electric heater, contained the mercury, and the whole was well lagged. A small coil of enamelled nichrome wire actually in the mercury supplied a fine adjustment. The subsidiary current was switched on and off by means of a relay connected to a mercury thermometer with a large bulb. The coil was supported on a spiral of thick iron wire at a distance of about 2 mm. from the bulb of the controlling thermometer. With a current of .4 amp. the period of the relay was from 20 to 30 seconds, and the temperature was kept constant to $.1^\circ \text{C}$. In spite of the lagging, however, there were variations in the temperature of the mercury in different parts of the thermostat, the extreme readings differing by $.15^\circ$. The temperature was therefore known to $.25^\circ$.

The procedure in the case of rubidium was exactly the same as for caesium.

Before the commencement of the experiment the calibration of the gauge was checked and found to be correct.

RESULTS.

Vapour Pressure of Cesium.

Equation (1) becomes

$$1.863 = T(11.52 p_{\text{Cs}} + \Sigma p M^{1/2} + 3.361 \cdot 10^{-3}),$$

where p_{Cs} is the vapour pressure of caesium and $\Sigma p M^{1/2}$ is the residual gas term.

Initial residual gas pressure.

$$T = 384. \quad 1.863 = 384(\Sigma p M^{1/2} + 3.361 \cdot 10^{-3}).$$

$$\therefore \Sigma p M^{1/2} = 1.491 \cdot 10^{-3}.$$

Final residual gas pressure

$$T = 377.8, \text{ whence } \Sigma pM^{1/2} = 1.571 \cdot 10^{-3}.$$

$$\text{Mean value } 1.531 \cdot 10^{-3}.$$

Therefore we have for the determination of the vapour pressure of cæsium the equation

$$\begin{aligned} 1.863 &= T(11.52 p_{Cs} + 1.531 \cdot 10^{-3} + 3.361 \cdot 10^{-3}) \\ &= T(11.52 p_{Cs} + 4.894 \cdot 10^{-3}). \end{aligned}$$

The value of p_{Cs} given in the second column, Table III., corresponds to the pressure of the vapour in the gauge which is at a temperature of about 150° . We get the true value of the vapour pressure from this by multiplying by $\sqrt{\frac{\theta}{\theta'}}$, where θ is the temperature of the thermostat and θ' the temperature of the fibre manometer.

In the case of rubidium the initial and final values of $\Sigma pM^{1/2}$ were $1.213 \cdot 10^{-3}$ and $1.559 \cdot 10^{-3}$. The equation for determining the vapour pressure becomes therefore

$$1.863 = T(9.244 p + 4.747 \cdot 10^{-3}).$$

The results are given in Table IV.

Calculation of Chemical Constants.

The graph shows the observed values of $\log p$ plotted against $\frac{1}{T}$ absolute. For comparison the values of $\log p$ at higher temperatures obtained by Hackspill ('Recherches sur les Métaux Alcalins,' p. 65: Paris, Gauthier Villars), are also shown.

The points lie very closely on two straight lines—showing that the specific heats of the liquid metals are practically constant over the range considered. As the observations were made at comparatively low temperatures it was deemed justifiable to extrapolate linearly to find the vapour pressure at the melting-point and hence the chemical constants of the two metals.

TABLE III.—Vapour Pressure of Cæsium.

T (seconds).	p (mm. of Hg).	θ Abs.	θ' Abs.	p' $\left(=p\sqrt{\frac{\theta}{\theta'}}\right)$	$\log p'$.	$\log p'$ Calc.	Error.
1	$4.43, 10^{-5}$	321.4	424.5	$3.85, 10^{-5}$	-4.4145	-4.421	.0065
2	8.01	330	424.3	7.07	-4.1503	-4.117	.0336
3	$2.04, 10^{-4}$	341.1	424.3	$1.83, 10^{-4}$	-3.7375	-3.746	.0085
4	3.40	348.5	424.0	3.08	-3.5114	-3.513	.0016
5	4.71	352.5	423.5	4.30	-3.3665	-3.391	.0245
6	8.49	362.2	423.5	7.86	-3.1046	-3.106	.0014
7	$1.93, 10^{-3}$	374.0	423.8	$1.81, 10^{-3}$	-2.7423	-2.779	.0367
8	3.38	386.6	424.0	3.23	-2.4908	-2.452	.0388

TABLE IV.—Vapour Pressure of Rubidium.

T (seconds).	p (mm. of Hg).	θ Abs.	θ' Abs.	p' $\left(=p\sqrt{\frac{\theta}{\theta'}}\right)$	$\log p'$.	$\log p'$ Calc.	Error.
1	$5.20, 10^{-5}$	364.5	424.2	$5.61, 10^{-5}$	-4.2510	-4.2162	.0348
2	$1.025, 10^{-4}$	371.3	426.1	$1.10, 10^{-4}$	-3.9586	-4.0046	.0460
3	1.59	378.0	426.0	1.69	-3.7721	-3.8037	.0316
4	2.13	384.7	424.8	2.24	-3.6498	-3.6098	.0400
5	2.86	388.1	425.2	3.00	-3.5229	-3.5139	.0090
6	4.86	395.2	425.5	5.04	-3.2976	-3.3191	.0215
7	5.31	397.8	426.3	5.0	-3.2596	-3.2494	.0101
8	6.25	400.0	426.3	6.45	-3.1904	-3.1913	.0009

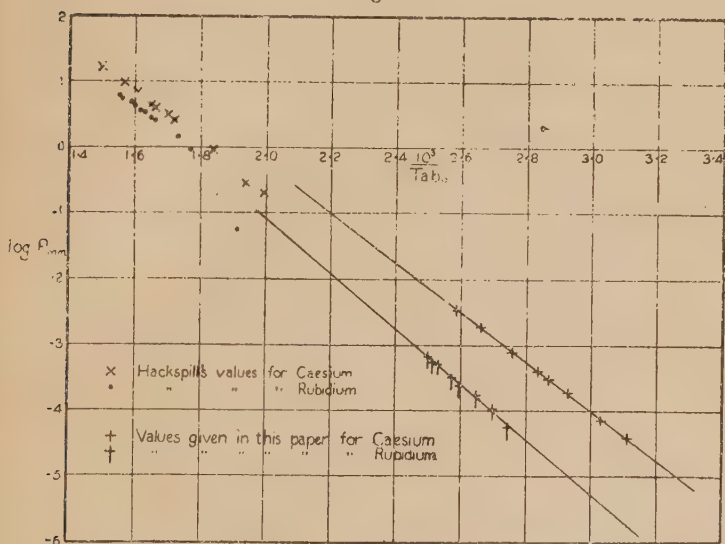
Assuming that $\log p = k - \frac{a}{T}$, the most probable values of k and a can be worked out—giving for cæsium

$$\log p = 7.256 - \frac{3753}{T},$$

and for rubidium

$$\log p = 7.331 - \frac{4209}{T}.$$

Fig. 2.



The values of $\log p$ calculated on this formula for the various values of T are given in the sixth column in the Tables III. and IV., and the differences between them and the observed value in the last column.

The method employed in the calculation of the chemical constants is similar to that developed by Egerton (Phil. Mag. Jan. 1920, p. 1).

We have from the Clausius-Clapeyron relation

$$\log_e p = -\frac{\lambda_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T (C_p - c_p) dT + i,$$

where C_p = atomic heat of vapour,

c_p = atomic heat of solid,

λ_0 = molecular latent heat at absolute zero.

In Egerton's paper it is shown that for the purposes of integrating the second term on the right-hand side of this equation, it is sufficiently accurate to put $c_p = c_v + aT^{3/2}$, where a is a constant.

If we take $c_p = c_v + aT^{3/2}$ and $C_p = \text{const} = 4.963$ and transform the logarithms to the base 10, we get

$$\log p = -\frac{\lambda_0}{4.571 T} + 2.5 \log T - \frac{1}{4.571 T} F - 0.0583 a T^{3/2} + C, \quad \dots (3)$$

where $F = T \int_0^T \frac{1}{T^2} \int_0^T c_v dT$, and C is the chemical constant.

Also for the molecular latent heat at the melting-point we have

$$\lambda_T = \lambda_0 + \int_0^T (C_p - c_p) dT - f_m,$$

where f_m = latent heat of fusion at melting-point.

Substituting for C_p and c_p , as before, we find

$$\lambda_0 = \lambda_T - 4.963 T + E + f_m + \frac{2}{5} a T^{5/2}, \quad \dots (4)$$

where $E = \int_0^T C_v dT$.

The values of $\frac{E}{T}$ and $\frac{F}{T}$ on Debye's formula for various values of $\frac{\beta\nu}{T}$ are tabulated in Nernst's 'Die Theoretischen und Experimentellen Grundlagen des Neuen Warmesatzes.'

Certain difficulty attends the determinations of the value of $\beta\nu$ for caesium and rubidium, and until figures are available which give the accurate values of the specific heats of these metals at low temperatures it will not be possible to calculate the chemical constant with accuracy from the vapour pressure measurements given in this paper.

The only values available are those given by Dewar (P. R. S. lxxxix. p. 158 (1913)), who found that at 50° Abs. $C_p = 6.05$ for rubidium and 6.82 for caesium. Using the correction formula $c_p = c_v + c_p^2 \frac{T}{T_s} A_0$ the corresponding values of C_v are found to be 5.92 and 6.65 respectively.

The value 6.65 is of no use since it is greater than 3R and the value 5.92 gives a value for $\beta\nu$ for rubidium about

a fifth of that obtained from the Lindemann melting-point formula. The probable explanation that these values of the atomic heat are so much higher than one would expect is that the metal still contained an appreciable quantity of hydrogen or other impurity at the time of the experiment.

Measurements have been made, however, on the Atomic Heat of Sodium at Low Temperatures (E. H. Griffiths & Ezer Griffith, *Phil. Trans.* cxiv. p. 348 (1914), and Günther, *Annalen der Physik*, lxiii. p. 476 (1920)). If the value of $\beta\nu$ for sodium is calculated from these measurements we can work out the constant k in the Lindemann melting-point formula

$$\nu = k \sqrt{\frac{T_s}{mv^{2.3}}}$$

and then work back to the values of $\beta\nu$ for cæsium and rubidium. This should give a fairly accurate value, for if the constant is suitably chosen the formula holds tolerably well for members of the same group of elements. Unfortunately there is a serious discrepancy between the two series of observations. The value of the constant k corresponding to Griffith's value of $\beta\nu$ for sodium is $2.6 \cdot 10^{12}$, while that corresponding to Günther's value is $2.0 \cdot 10^{12}$. In view of this discrepancy and the absence of any data for cæsium and rubidium themselves, the values of $\beta\nu$ used in the following calculations of the chemical constants were obtained by using in the melting-point formula the constant $2.8 \cdot 10^{12}$ —which is the value giving the best results when all the elements are considered.

The specific heats of both cæsium and rubidium have been measured at room temperature and can be used to determine " α " in the correction formula $C_p = C_v + \alpha T^{3/2}$.

The values of f_m , the molecular latent heats of fusion, are given by Rengarde (*Comptes Rendus*, clvi. p. 1897 (1913)).

Chemical Constant of Cæsium.

$$\beta\nu = 49.5. \quad T_m = 301.25.$$

From the vapour measurements in this paper

$$\log p = 7.256 - 3753/T.$$

$$\text{At the melting-point } \lambda_{T_m} = RT_m^2 \frac{d}{dT} (\log p) = 17155,$$

$$4.963 T_m = 1496.$$

At 0°C , $C_p = 6.396$,

$$\frac{\beta\nu}{T} = 0.181, \quad \therefore C_p = 5.94,$$

$$\text{but } C_p = C_v + aT^{3/2}.$$

$$\therefore a = 8.72 \cdot 10^{-5}.$$

At the melting-point $\frac{\beta\nu}{T_m} = 0.164, \quad \therefore \frac{E}{T} = 5.596,$

$$\text{and } E = 1686.$$

$$.4 aT^{5/2} = 55,$$

$$f_m = 500.$$

Substituting in equation (4) we get $\lambda_0 = 17895$.

At the melting-point we have $\frac{\lambda_0}{RT_m} = 12.995,$

$$2.5 \log T_m = 6.192,$$

$$\frac{F}{T} = 13.25, \quad \frac{F}{RT} = 2.898,$$

$$\log p = 7.256 - 3753/T = -5.202 \text{ mm.} = -8.032 \text{ atmospheres.}$$

$$.0583 aT^{3/2} = .027.$$

In working out the probable error of the result it is assumed that T_m is known to $.1^\circ$ and that the latent heat of fusion per gramme is known to $.1$ calorie. The probable errors of λ_{T_m} and $\log p_m$ are worked out from the errors in column 8, Table III., and therefore take into account the probable error in the observation of the temperature of the thermostat. An error of 5 per cent. is allowed for in the determination of $\beta\nu$ from the melting-point formula.

Substituting in equation (3) we now have

$$12.995 \pm .077 \qquad 6.198 \pm .001$$

$$2.898 \pm .068 \qquad 8.082 \pm .018$$

$$.027$$

$$15.920 \pm .145 \qquad 14.280 \pm .019$$

$$14.280 \pm .019$$

$$C = \underline{1.640 \pm .164}$$

Chemical Constant of Rubidium.

$$\beta\nu = 68\cdot1. \quad T_m = 311\cdot5.$$

From the vapour pressure measurements

$$\log p = 7\cdot331 - 4209/T.$$

At the melting-point $\lambda_{T_m} = 19239$,

$$4\cdot963 T_m = 1545,$$

$$\frac{\beta\nu}{T} = 0\cdot219, \quad \text{whence} \quad E = 1708.$$

$$\text{At } 0^\circ \text{C.} \quad C_p = 6\cdot85, \quad \frac{\beta\nu}{T} = 0\cdot249. \quad \therefore C_v = 5\cdot94$$

$$a = 2\cdot01 \cdot 10^{-4},$$

$$\cdot4 a T^{5/2} = 138,$$

$$f_m = 525,$$

$$\therefore \text{from equation (4)} \quad \lambda_0 = 20054.$$

$$\text{At the melting-point} \quad \frac{\lambda_0}{RT_m} = 14\cdot084,$$

$$2\cdot5 \log T_m = 6\cdot234,$$

$$\frac{F}{T} = 11\cdot52, \quad \therefore \frac{F}{RT} = 2\cdot520,$$

$$\cdot0583 a T^{3/2} = \cdot058,$$

$$\log p = 7\cdot331 - 4209/T = -6\cdot181 \text{ mm.} = -9\cdot062 \text{ atmospheres.}$$

Working out the probable errors of each term in the same way as for the cæsium and substituting in equation (3) we have

$14\cdot084 \pm \cdot098$	$9\cdot062 \pm \cdot024$
$2\cdot520 \pm \cdot061$	$6\cdot234 \pm \cdot001$
$\cdot058$	
$16\cdot662 \pm \cdot159$	$15\cdot296 \pm \cdot025$
$15\cdot296 \pm \cdot025$	
$C = 1\cdot366 \pm \cdot184$	

If $C = 1\cdot5 \log M + C_0$, where M is the molecular weight, the corresponding values of the absolute constant C_0 are $-1\cdot545 \pm \cdot164$ and $-1\cdot532 \pm \cdot184$. The value calculated

from the constants h and k is -1.608 , so that the results are in agreement within the error.

The equation $\log p = k - \frac{a}{T}$ obtained from the vapour pressure measurements may also be used to give an approximation by a rather long extrapolation to the value of λ at the boiling-point, from which Trouton's coefficient $\frac{\lambda_{T_B}}{T_B}$ (where T_B is the boiling-point) can be determined. The values obtained are 18.2 for caesium and 19.9 for rubidium.

Discussion of Results.

As the results for the chemical constants of both metals are both higher than the theoretical value by roughly the same amount, it seems probable that there is some other source of error not yet considered.

The true values of $\beta\nu$ may possibly be higher than those used in the above calculation, or if they are taken as correct the high values of the chemical constant suggest that the individual measurements of the vapour pressures are also all too high.

This may be due to two causes :

(1) The caesium or rubidium might have given up an appreciable quantity of gas after the apparatus was finally sealed off, and re-absorbed a certain amount of it each time it was cooled in CO_2 snow and ether. The pressure of hydrogen required to produce an increase of .07 in the chemical constant is of the order 10^{-3} mm. in excess of that given by the "residual gas pressure" determinations ; and a correspondingly smaller amount of any other gas of larger molecular weight would produce the same effect.

(2) The trap immersed in liquid air might have allowed a certain amount of mercury vapour to pass through during calibration. This would have made the observed times T too small and in consequence the calculated value of the constant b in equation (1) would be too large. Pressures re-calculated from the formula would therefore also be too large.

In order to test the efficiency of the trap the following experiment was carried out. The fibre manometer, calibrated in the usual way with the trap in liquid air, was used to measure the amount of mercury vapour passing through the trap when it was cooled in CO_2 snow and ether instead of in liquid air. Two series of readings were taken, one with the trap empty, the other when it was filled with copper

turnings, in order to increase the cold surface exposed to the gas. The trap was found to be somewhat more efficient when full of copper turnings than when empty. A third series of readings were taken with the trap full of copper turnings immersed in liquid air. This series was found to be in complete accord with the calibration readings, which means that the trap, if immersed in liquid air, stops as much mercury vapour when it is empty as when it is full of copper turnings. This shows that the trap may be regarded as perfectly efficient when immersed in liquid air.

It seems unlikely that the metal should give up so much gas after the care taken over its distillation into the apparatus, and therefore the probable source of the error is the uncertainty of the value of βv .

The actual amounts of mercury vapour which passed through the trap when it was immersed in CO₂ snow and ether were surprisingly large, and it is therefore thought desirable to give the results of the experiment in detail.

Two traps of the shape shown in fig. 1 were used. The dimensions were as follows :—

	Trap I.	Trap II.
Internal diameter of outside tube	2 cm.	1·8 cm.
„ „ „ inside „	·9 cm.	·8 cm.
Height between bottom of inside tube and surface of cooling liquid	12·3 cm.	11·2 cm.

Trap I. was, unfortunately, broken after the 1st series of readings, before it was filled with copper turnings. The results are, however, given because they agree remarkably well with those obtained from Trap II. when empty, although the dimensions of the traps are different.

The fibre manometer employed was the same as that used for the determination of the vapour pressures of cesium and rubidium. It was re-calibrated at room temperature in the ordinary way with the trap in liquid air. The values found for the constants a and b in equation (1) were

$$b = 1·780,$$

$$a = 3·116 \cdot 10^{-3}.$$

The values at 150° C. were

$$b = 1·863,$$

$$a = 3·361 \cdot 10^{-3},$$

showing that the constants change slightly with the temperature.

The results for the various series of readings are given in Tables V., VI., and VII.

TABLE V.

Amount of Mercury Vapour let through by Trap I., empty.

T, seconds.	p, air pressure.	π , pressure of mercury vapour.
82.7	$3.02 \cdot 10^{-3}$	$1.52 \cdot 10^{-4}$
118	1.59	2.39
131	1.38	2.17
156	1.09	1.71
176.3	.884	1.56
222	.405	1.94
300.7	.047	1.78
Mean $1.87 \cdot 10^{-4}$		

TABLE VI.

Amount of Mercury Vapour let through by Trap II., empty.

T, seconds.	p, air pressure.	π , pressure of mercury vapour.
75.7	$3.32 \cdot 10^{-3}$	$1.78 \cdot 10^{-4}$
111	1.91	1.86
120	1.72	1.74
162	.97	1.86
174	.87	1.71
289	$< 10^{-5}$	2.12
Mean $1.84 \cdot 10^{-4}$		

TABLE VII.

Amount of Mercury Vapour let through by Trap I.
when filled with Copper Turnings.

T, seconds.	p, air pressure.	π , pressure of mercury vapour.
70.0	$3.79 \cdot 10^{-3}$	$1.36 \cdot 10^{-4}$
127	1.73	1.14
152	1.28	1.21
176	1.02	1.06
204	.77	.98
214	.63	1.49
277	.33	1.06
380	$< 10^{-5}$	1.10
Mean $1.17 \cdot 10^{-4}$		

It will be seen that the trap, when cooled in CO_2 snow and ether, lets through an amount of mercury vapour which is roughly constant for air pressures from $5 \cdot 10^{-3}$ mm. downwards. The mean values for Traps I. and II. empty are $1 \cdot 87 \cdot 10^{-4}$ and $1 \cdot 8 \cdot 10^{-4}$ mm. respectively, and for Trap II. full of copper turnings $1 \cdot 17 \cdot 10^{-4}$ mm.

The experiment was conducted at room temperature (about $14^\circ \text{C}.$), and as the vapour pressure of mercury at this temperature is about $8 \cdot 10^{-4}$, the figures show that the trap allows mercury to pass through up to 23 per cent. of the vapour pressure when it is empty and up to 15 per cent. when it is full of copper turnings.

SUMMARY.

(1) A slightly modified form of Haber's vibrating quartz fibre manometer is described.

(2) The vapour pressure of mercury is measured at room temperature. The mean of the results, corrected to $20^\circ \text{C}.$, is $1 \cdot 30 \cdot 10^{-3}$ mm.

(3) The vapour pressures of cæsium and rubidium at various temperatures between $50^\circ \text{C}.$ and $130^\circ \text{C}.$ are measured. The relation between $\log p$ and $1/T$ is found to be approximately linear over the range considered, and the results can be represented by the formulæ

$$\log p = 7 \cdot 256 - 3753/T \quad \text{for cæsium,}$$

$$\text{and} \quad \log p = 7 \cdot 331 - 4209/T \quad \text{for rubidium.}$$

(4) The chemical constants of the two metals are calculated; the values obtained are $1 \cdot 64(0) \pm 1 \cdot 6(4)$ for cæsium and $1 \cdot 36(6) \pm 1 \cdot 8(4)$ for rubidium. If $C = 1 \cdot 5 \log M + C_0$, where M is the molecular weight, the values obtained for the absolute chemical constant C_0 are $-1 \cdot 54(5) \pm 1 \cdot 6(4)$ and $-1 \cdot 53(2) \pm 1 \cdot 8(4)$. The theoretical value of C_0 is $-1 \cdot 608$, so that the results are in agreement within the error.

(5) The value of Trouton's coefficient $\frac{\lambda_{\text{TB}}}{T_{\text{B}}}$ (where T_{B} is the boiling-point) is worked out; giving 18.2 for cæsium and 19.9 for rubidium.

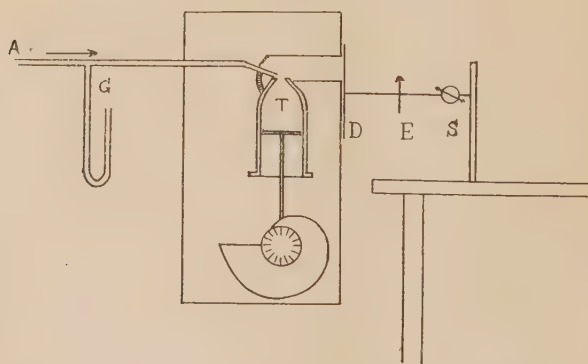
(6) The chemical constants for both metals are above the theoretical value. The possible reasons for this are discussed.

(7) Some measurements are made on the amount of mercury vapour passing through a trap of the ordinary type when cooled in CO_2 snow and ether. The mean value is found to be $1.84 \cdot 10^{-4}$ mm. It is shown that the trap is more efficient when filled with copper turnings; the mean value in this case being $1.17 \cdot 10^{-4}$. When the trap is cooled in liquid air the readings with and without copper turnings in the trap are in complete agreement.

IV. *On the Critical Frequency of Pulsation of Tones.* By MOLLIE WEINBERG, M.A., M.Sc., Research Student of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, and FRANK ALLEN, Ph.D., F.R.S.C., Professor of Physics, University of Manitoba*.

THE successful application of the principle of the persistence of vision, or the critical frequency of flicker, to the study of problems of colour vision suggested the probable value of the analogous principle of the persistence of audition to the solution of problems of the perception of sound. In this communication the results of some investigations based on this latter principle are described, which show that the method is capable of extension to some of the phenomena of physiological acoustics.

Fig. 1.



The experimental arrangements, fig. 1, were similar to those used in investigations in Colour Vision†.

* Communicated by the Authors. Read at the meeting of the Royal Society of Canada, Ottawa, May 1922.

† Phys. Rev. vol. xi. p. 257 (1900); Phil. Mag. vol. xxxviii. p. 55 (1919).

The source of sound was a Stern Tonvariator, T, placed inside a box lined with very soft thick felt, through which at a suitable place a hole was cut. The tonvariator was blown by a stream of air from a large constant-pressure tank, and the pressure was further regulated by suitable cocks, and measured by a small water-gauge, G. The periodic interruption of the continuous sound into separate pulses was effected by the rotation of a light aluminium disk, D, with four symmetrically placed holes of the same size as that in the box. For this purpose an electric motor was used, which was connected with a storage battery to secure exact regulation of the speed. A speed counter, S, making electric contact every fiftieth revolution of the disk, and a clock beating half seconds, were connected with a chronograph from which the speed of the disk, and hence the critical frequency of pulsation, or flutter, of the sound was computed when it became just continuous to the ear.

The ideal disk should completely interrupt the sound ray except when its openings coincide with that in the box from which the sound is issuing. To secure this, the disk might be made of the most inelastic material possible. But it is also essential that it should be very light, to permit rapid adjustment for the critical frequency of pulsation, or flutter, of the sound. A thin aluminium disk was chosen, as stated above, which was covered with velvet to dampen the vibrations as far as possible. The velvet served another purpose also, since the disk could be placed so close to the box that the velvet pile just grazed its surface. It is remarkable how greatly the intensity of the sound escaping between the box and the disk is lowered by eliminating the last slight distance between them. The ear of the observer—in this arrangement of apparatus the left was most conveniently used—was always placed in the same position, E, so that variations in the intensity of sound could not be attributed to any condition other than the rotation of the disk.

The tonvariator* is a simple König resonator with a movable bottom acting like a piston. To regulate the pitch of the tone, the piston is moved by a pin resting on the edge of a brass plate cut in a spiral of such a form that the frequencies may be read directly on an evenly-graduated circular disk rigidly attached to the spiral. The tonvariator was capable of giving pure tones of considerable variation in intensity covering the octave from 150 to 300 double vibrations per second. Since the frequencies of the tonvariator varied with

* *Physikalische Zeitschrift*, vol. v. p. 693 (1904).

the blowing pressure, it became necessary to obtain calibration curves from standard tuning forks. These curves were exact straight lines. The corrected frequencies ranged from 142 to 285 vibrations. The intensities were those obtained with air-pressures from 1.25 to 2.40 cm. of water. Above and below these pressures the tones were not sufficiently pure for experimental purposes.

The greatest care was taken to eliminate all extraneous noises in motor, disk, and chronograph. But it was found impossible with such arrangements as were available at the time to prevent some sound escaping from the surface of the box and through the disk. The rotation of the disk produced marked variation of the intensity of the sound ray, but the ideal sudden transition from silence to full intensity, as from darkness to light, was by no means realized. No doubt great improvements are possible in the control of sound, which we have found the most difficult part of the problem.

In making the measurements the tonvariator was adjusted to give a steady sound of the desired pitch and intensity. The ear was then placed at the proper place and the speed of the disk increased so that the interrupted pulses of sound became fused into a just continuous sensation. The chronograph circuits were then closed and the readings recorded. Each record gave several measurements, from which mean values of the critical frequency of pulsation were obtained. Each point on the curves is the mean of about ten measurements obtained from three or four independent determinations.

For each pressure or intensity of sound such measurements were made for seven frequencies extending through the octave. Ten pressures also were used between the limits mentioned above. These measurements are recorded in Table I., from which the corresponding normal curves are plotted in fig. 2. Each normal curve represents the relation between the vibration frequency, N , and the duration of the tone at the critical frequency of pulsation, D , for the octave mentioned, at a definite pressure or intensity of sound, P , when the ear was in its normal unfatigued condition. The ten normals form a regular family of curves, all being slightly convex toward the axis of frequencies.

The lowest curve of the group is that obtained with the least pressure or intensity of sound, and the highest with the greatest pressure or intensity. It has been shown by Love and Dawson* that the intensity of sound emitted by a

* Phys. Rev. vol. iv. p. 49 (1919).

TABLE I.

Normal Curves Corrected for Frequency.

N.	D.	P.	N.	D.	P.
A. 142.0	0.0185	1.25 cm.	F. 143.0	0.0206	1.82 cm.
164.0	.0172	"	167.0	.0192	"
186.0	.0160	"	190.0	.0182	"
208.0	.0149	"	214.0	.0170	"
230.0	.0139	"	237.0	.0161	"
252.0	.0130	"	260.5	.0153	"
264.0	.0127	"	284.0	.0146	"
B. 142.5	0.0194	1.45 cm.	G. 143.0	0.0210	1.98 cm.
165.5	.0181	"	167.0	.0195	"
187.5	.0168	"	190.0	.0184	"
210.0	.0157	"	214.0	.0173	"
235.0	.0146	"	237.0	.0163	"
256.7	.0137	"	260.5	.0154	"
278.0	.0130	"	284.0	.0148	"
C. 142.8	0.0197	1.53 cm.	H. 143.0	0.0211	2.10 cm.
165.8	.0184	"	167.2	.0200	"
188.8	.0172	"	190.2	.0187	"
211.8	.0161	"	214.2	.0177	"
235.7	.0152	"	237.2	.0166	"
257.9	.0143	"	260.7	.0158	"
280.5	.0138	"	284.2	.0151	"
D. 142.9	0.0201	1.62 cm.	I. 143.2	0.0212	2.20 cm.
166.2	.0187	"	167.3	.0203	"
189.0	.0177	"	191.0	.0190	"
212.0	.0166	"	214.6	.0180	"
235.3	.0155	"	238.0	.0171	"
258.2	.0146	"	261.2	.0160	"
280.9	.0140	"	284.2	.0155	"
E. 143.0	0.0203	1.70 cm.	J. 143.5	0.0215	2.40 cm.
166.6	.0190	"	168.2	.0205	"
189.7	.0179	"	191.2	.0192	"
213.2	.0168	"	215.0	.0184	"
236.2	.0158	"	238.3	.0173	"
259.3	.0149	"	261.9	.0163	"
283.0	.0143	"	285.0	.0156	"

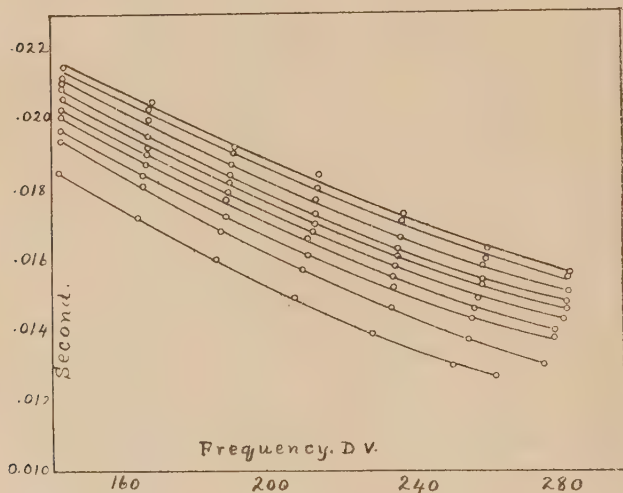
resonator is proportional to the blowing pressure. Assuming this to be true for the form of resonator used in this investigation, the curves in fig. 2 may be regarded as indicating definitely the relation between the vibration frequency, the duration of the tone at the critical frequency of pulsation, and the intensity of the tone.

It is worthy of remark that in the analogous normal persistency curves for spectra* of varying intensities the opposite condition prevails. With light the brightest colours give the lowest curve, that is, they have the smallest values

* Phil. Mag. vol. xxxviii. p. 81 (1919).

of the duration of the light at the critical frequency of flicker; whereas in sound the greatest intensities have the largest values of the duration of the tone at the critical frequency of pulsation. The mechanisms in the two sets of phenomena are widely different. Vision probably results from photo-electric action on the nerves; in sound the auditory nerves are excited by mechanical vibrations.

Fig. 2.



A somewhat similar investigation to that described above was made by Mayer*. His method was as follows: between a vibrating tuning fork and its resonator he interposed a revolving disk with openings of the same shape as that in the resonator, so that the sound was heard loudly when an opening in the disk came in front of that in the resonator, and faintly when the latter was covered. He found that his measurements conformed to the law

$$D = \frac{K}{N} + C,$$

where D is the duration of the tone at the critical frequency of pulsation, N the frequency of the fork, and K and C are constants.

The measurements given in Table I. were tested by this law and found, when plotted, not to give straight lines.

* Silliman's Journal, ser. 3, vol. viii. (1874); Helmholtz, 'Sensations of Tone' (Eng. Trans.), p. 417.

The graphs possessed a slight regular curvature very similar to that of the normal curves in fig. 2, but opposite in sign. No doubt the time of duration of the sound at the critical frequency of pulsation and the frequency of the tone are connected in some inverse relation. The precise nature of that function, as will later be discussed, appears to be

$$D = \frac{K}{\sqrt{\log N}} + C$$

where the letters D, N, K, C have the same significance as above.

The difference between Mayer's relation and that here obtained is probably due to his method of interposing a resonator between the source of sound and the ear, whereas in our experiments the fusion of sounds was effected in the ear directly. Another possible explanation of Mayer's results is given in a later communication, "On the Effect of Aural Fatigue" *.

It will be noticed in fig. 2 that the vertical distances between the normal curves are not equal. The interval between the curves for the highest intensities is small, and gradually increases as the intensity is decreased. This suggested the possibility that some law connecting the duration time at the critical frequency of pulsation and the intensity of the sound might be deduced.

In colour vision, Ferry† and Porter‡ found that the relation between the duration, D, of a flash of colour upon the retina at the critical frequency of flicker and the luminosity, L, was expressed by the equation

$$D = \frac{1}{K \log L}, \dots \dots \dots \text{(Ferry)}$$

or $n = K \log L + C \dots \dots \dots \text{(Porter)}$

where n is the reciprocal of D , and K and C are constants. This equation is independent of the wave-length of the light.

As we have seen, the intensities of sounds and their duration at the critical frequency of pulsation have a direct and not an inverse relationship, as is the case in colour vision. Several equations suggested by the above were tried without success.

* P. 126.

† Amer. Jour. Sci. (3), vol. xlv. p. 193 (1892).

‡ Proc. Roy. Soc. vol. lxx. p. 313 (1902).

That which appears to give the best result is

$$D = K \sqrt{\log P} + C$$

where D is the duration of the sound at the critical frequency of pulsation, P the blowing pressure to which the intensity of the sound is proportional, N the frequency of vibration of the tone, and K and C are constants.

In fig. 3, plotted from the values in Table II., the critical frequencies of pulsation are plotted against the square roots of the logarithms of the pressure. The resulting curves are, in all five cases, straight lines.

Fig. 3.

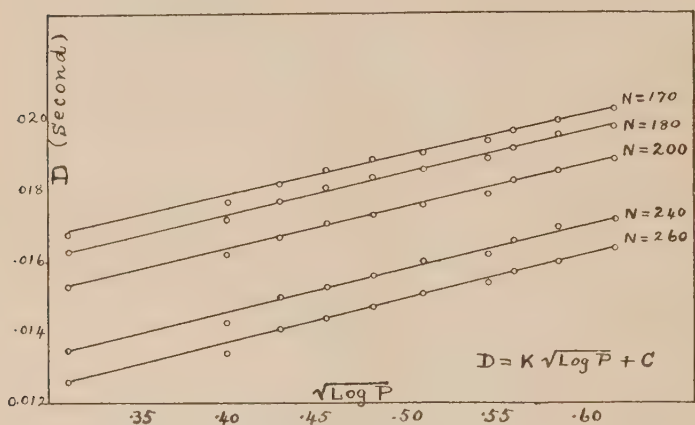


TABLE II.

Pressure P .	$\sqrt{\log P}$.	D.	D.	D.	D.	D.
		$N=170$.	$N=180$.	$N=200$.	$N=240$.	$N=264$.
		sec.	sec.	sec.	sec.	sec.
2.40 cm.	0.616	0.0203	0.0198	0.0189	0.0172	0.0164
2.20 "	.585	.0200	.0196	.0186	.0170	.0160
2.10 "	.560	.0197	.0192	.0183	.0166	.0157
1.98 "	.546	.0194	.0189	.0179	.0162	.0154
1.82 "	.510	.0191	.0186	.0176	.0160	.0151
1.70 "	.482	.0189	.0184	.0173	.0156	.0147
1.62 "	.456	.0186	.0181	.0171	.0153	.0144
1.53 "	.430	.0182	.0177	.0167	.0150	.0141
1.45 "	.401	.0177	.0172	.0162	.0143	.0134
1.25 "	.0311	.0168	.0163	.0153	.0135	.0126

A further test was made. The tonvariator was maintained constant at three different frequencies in succession, and the pressures adjusted for eight successive values in each case. The frequencies used were 170, 200, and 240 vibrations.

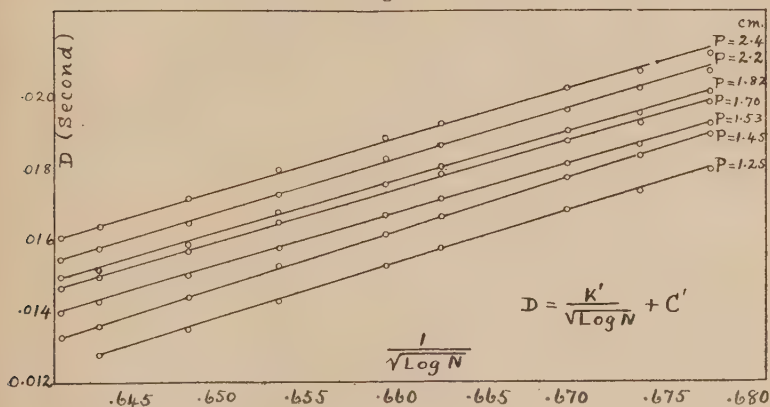
The data obtained are incorporated in Table II. with those for the same frequencies taken from the normal curves. The straight lines in fig. 3 are therefore the result, not only of data taken from the normal curves, but also of data obtained directly from independent measurements. This forms a more complete verification of the law that, at the critical frequency of pulsation, the duration of a pulse of sound varies directly as the square root of the logarithm of the pressure or intensity.

Further investigations were made concerning the relation between the critical frequency of pulsation, D , and the frequency of the tone, N , when the pressure remained constant. It will be remembered that Mayer had expressed that relation in the form

$$D = \frac{K}{N} + C.$$

On applying new data obtained in this investigation, the above law does not hold. The only manner in which Mayer's

Fig. 4.



equation agrees with data here obtained is in the fact that both indicate an inverse relationship. The precise nature of this inverse function was not at first apparent. After trying a number of equations, however, we find the one that appears to give the best results to be

$$D = \frac{K'}{\sqrt{\log N}} + C'$$

where D and N have same meaning as previously, and K' and C' are arbitrary constants. In fig. 4, plotted from the

data in Table III., the time values of the critical frequencies of pulsation are plotted against the reciprocals of the square roots of the logarithms of the frequencies, and again, the results are seen to be very consistent straight lines.

TABLE III.

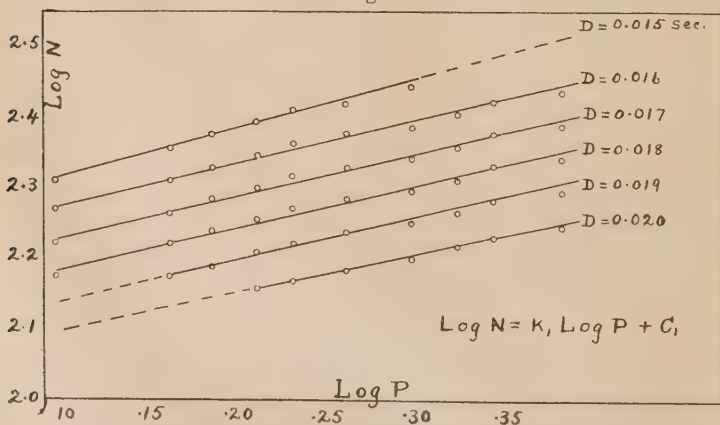
N.	$\frac{1}{\sqrt{\log N}}$	D.	D.	D.	D.	D.	D.	D.
		P= 2.40 c. sec.	P= 2.10 c. sec.	P= 1.82 c. sec.	P= 1.70 c. sec.	P= 1.53 c. sec.	P= 1.45 c. sec.	P= 1.25 c. sec.
150	0.6779	0.0213	0.0208	0.0202	0.0199	0.0193	0.0190	0.0180
160	.6739	.0208	.0203	.0196	.0194	.0187	.0184	.0174
170	.6698	.0203	.0197	.0191	.0189	.0182	.0177	.0168
190	.6627	.0193	.0187	.0181	.0179	.0172	.0167	.0158
200	.6596	.0189	.0183	.0176	.0173	.0167	.0162	.0153
220	.6536	.0180	.0173	.0168	.0165	.0158	.0153	.0143
240	.6485	.0172	.0166	.0160	.0156	.0150	.0143	.0135
260	.6435	.0164	.0158	.0152	.0150	.0143	.0136	.0128
270	.6414	.0161	.0155	.0150	.0147	.0140	.0133	...

It is very interesting to note that whereas D varies directly as the root of the logarithm of P when N remains constant, it varies inversely as the root of the logarithm of N when P remains constant. The square root of the logarithm seems to be involved in both relations.

This suggested the possibility of some simple relationship existing between N and P at a constant value of the frequency of pulsation, D . For this purpose, horizontal cross-sections were taken through the family of curves in fig. 2. Again, after many attempts had been made, the following equation seemed to give the best results:

$$\log N = K'' \log P + C'',$$

Fig. 5.



In fig. 5, values taken from Table IV., the logarithms of the frequencies were plotted against the logarithms of the

pressures. The resulting lines, although not as consistently straight as those representing the other relations, seem to verify the equation.

TABLE IV.

P.	Log P.	N.	Log N.	N.	Log N.	N.	Log N.
		D=0·0150 sec.		D=0·0160 sec.		D=0·0170 sec.	
1·25 cm.	0·0969	205	2·312	186	2·270	167	2·223
1·45 "	·1614	226	2·354	204	2·310	184	2·265
1·53 "	·1847	239	2·378	214	2·330	193	2·286
1·62 "	·2095	248	2·394	223	2·348	201	2·303
1·70 "	·2305	259	2·413	231	2·364	208	2·318
1·82 "	·2601	263	2·420	238	2·377	214	2·330
1·98 "	·2967	276	2·441	244	2·387	220	2·342
2·10 "	·3222	254	2·405	228	2·358
2·20 "	·3424	265	2·423	238	2·377
2·40 "	·3802	273	2·436	244	2·387
		D=0·0180 sec.		D=0·0190 sec.		D=0·0200 sec.	
1·25 cm.	0·0969	150	2·176
1·45 "	·1614	167	2·223	150	2·176
1·53 "	·1847	174	2·241	155	2·190
1·62 "	·2095	181	2·258	162	2·210	144	2·158
1·70 "	·2305	187	2·272	167	2·223	148	2·170
1·82 "	·2601	193	2·286	173	2·238	153	2·185
1·98 "	·2967	198	2·297	178	2·250	158	2·199
2·10 "	·3222	205	2·312	184	2·265	165	2·217
2·20 "	·3424	214	2·330	192	2·283	171	2·233
2·40 "	·3802	220	2·342	197	2·294	176	2·246

The three laws, therefore, which we have tentatively deduced are :—

$$D = K \sqrt{\log P} + C ; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$D = \frac{K'}{\sqrt{\log N}} + C' ; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\log N = K'' \log P + C'' . \quad . \quad . \quad . \quad . \quad (3)$$

Were it not that the C's in equations (1) and (2) are apparently different, the two equations might be put together in the form

$$D = K \frac{\sqrt{\log P}}{\sqrt{\log N}} .$$

This equation would define an acoustical surface, analogous in many respects to the well-known thermo-dynamic surface, each point on this acoustical surface denoting a relation between the pressure or intensity, the frequency of the tone, and its critical frequency of pulsation.

The above is an interesting conjecture, which might lead, on fuller investigation, to fruitful results.

The range of pressures and frequencies in this investigation was small, and before the above "laws" can be accepted with confidence they should be tested through a far greater range of intensities and frequencies than the apparatus used in this investigation afforded.

An attempt was made to determine whether normal measurements of other observers correspond with those here obtained, *i. e.*, whether the sensitivity to intensity and the duration of tones are the same for the average ear. Normal curves of four other observers have so far been obtained. These are shown in fig. 6, with the data from which they were plotted in Table V.

Fig. 6.

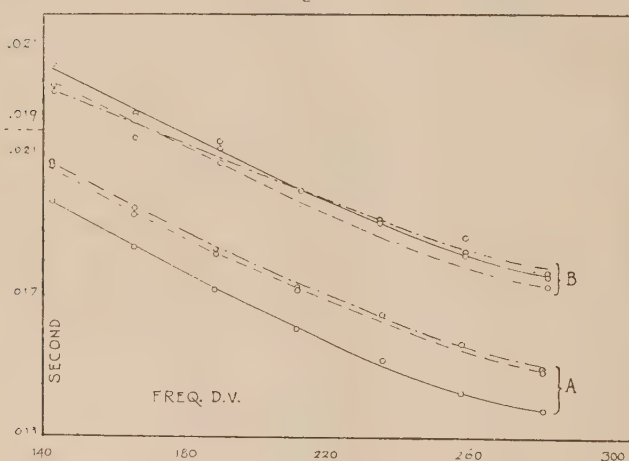


TABLE V.

Normal Curves of Other Observers.

A. N. D. (M.W.).			P. D. (E.W.).			D. (H.W.).	
	Second.			Second.			Second.
142.8	0.0197	1.53 cm.	1.53 cm.	0.0207	1.53 cm.		0.0208
165.8	.0184	"	"	.0193	"		.0195
188.8	.0172	"	"	.0182	"		.0184
211.8	.0161	"	"	.0172	"		.0173
235.7	.0152	"	"	.0165	"		.0165
257.9	.0143	"	"	.0157	"		.0157
280.5	.0138	"	"	.0149	"		.0150
B. (M.W.).			(S.G.L.).			(A.H.).	
	Second.			Second.			Second.
143.0	0.0206	1.98 cm.	1.88 cm.	0.0200	1.90 cm.		0.0198
166.0	.0192	"	"	.0185	"		.0191
190.0	.0182	"	"	.0178	"		.0184
213.0	.0170	"	"	.0165	"		.0170
236.0	.0161	"	"	.0162	"		.0162
259.0	.0153	"	"	.0152	"		.0157
282.0	.0146	"	"	.0143	"		.0147

The broken line and the dot-dash curves are those of the other observers ; the continuous curves are those of one of the authors (Weinberg) and are inserted for the sake of comparison. The data are also given in Table V.

The curves are divided into two groups ; those in group A were obtained at approximately the same pressure or intensity ; those in group B at different pressures or intensities.

The general slope of all the curves in both groups is very nearly the same. The very slight difference in curvature of the two curves in group B, as seen by their intersection at a very minute angle, may perhaps be attributed to the inexperience of the other observers.

Assuming the ears of all the observers to be average, this approximate sameness of the general slope may be taken to indicate that the degree of decrease in the duration of a tone, as its vibration frequency or pitch becomes higher, is very nearly the same for the average ear.

The relative vertical displacement of the curves in group A indicates that so-called normal ears are not equally sensitive to sounds of the same intensity, since the duration of tones of the same pitch at the critical frequency of pulsation differs.

In similar investigations in colour vision it was found that in persons between about eighteen and fifty-five years of age the sensitivity of normal eyes to the intensity of illumination is the same*. In audition, however, the sensitivity of the average ear to the intensity of tone varies. This difference is very probably due to the wide difference in the character of the two mechanisms or processes involved. The perception of light is most probably a photo-electric or chemical effect—a reaction of atoms and molecules to the stimulation of light-waves. Hence it is to be expected that for a constant intensity of stimulation there would be approximately constant atomic interactions, *i. e.*, approximately constant sensitivity. In the case of audition, however, the instrument of tone perception, the ear, is an extremely complicated mechanical structure, and therefore subject to many sources of defect or of difference. And in a mechanism so minute and delicate as the ear, it would be little less than miraculous were the mass, elasticity, and other physical properties of its component parts found always to be the same†.

* Ferry, *Am. Journ. Sci.* vol. xlv. (1892).

† Seashore, 'Psychology of Musical Talent,' p. 81.

We desire to express our thanks to Prof. J. C. McLennan, F.R.S., of Toronto University, for the loan of Standard König Tuning Forks used for calibration of the tonvariator.

This research was conducted under the auspices of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, to which body we also desire to express our thanks.

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V. *Tables of Bessel Functions.* By HUGH E. H. WRINCH, M.I.Mech.E., and DOROTHY WRINCH, D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London*.

THE present paper contains further tables of the Bessel Functions.

The Bessel Functions† $J_n(x)$ and $I_n(x)$ may be defined for integer values of n by

$$J_n(x) = \frac{x^n}{2^n \Gamma(n+1)} \left\{ 1 - \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} - \dots \right\},$$

$$I_n(x) = \frac{x^n}{2\Gamma(n+1)} \left\{ 1 + \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} + \dots \right\}.$$

For large real values of x , $I_n(x)$ has the asymptotic expansion,

$$I_n(x) = \frac{e^x}{(2\pi n)^{\frac{1}{2}}} \left\{ 1 + \frac{1^2 - 4n^2}{1! 8x} + \frac{(1^2 - 4n^2)(3^2 - 4n^2)}{2! (8x)^2} + \dots \right\}.$$

It possesses the recurrence formula,

$$I_{n-1}(x) - I_{n+1}(x) = \frac{2n}{x} I_n(x).$$

Note.—We are indebted to the Trustees of the Dixon Fund of the University of London for a grant in aid of the computations contained in this paper and in the two preceding papers (Proc. Roy. Soc. ci. pp. 493–528) (1922); Phil. Mag. xlv. pp. 846–849 (1923)).

* Communicated by the Authors.

† For an extensive bibliography of the subject, see G. N. Watson's 'Theory of Bessel Functions' (1923).

Tables of Bessel Functions.

TABLE I.

x .	$I_0(x)$.	$I_1(x)$.	$I_2(x)$.	$I_3(x)$.	$I_4(x)$.	$I_5(x)$.	$I_6(x)$.
16	893440	865053	785307	668728	534531	401459	283630
17	235494	228461	208619	179376	145312	110995	800203
18	621838	604316	554688	481050	394347	305785	224460
19	164461	160075	147611	128999	106877	839964	626673
20	435585	424553	393127	345926	289351	230188	174262
21	115514	112729	104777	927709	782714	629533	482942
22	306695	299639	279451	248828	211592	171889	133458
23	815139	797224	745822	667516	571676	468661	367918
24	216863	212294	199168	179103	154397	127636	101214
25	577452	565783	532191	480634	416834	347243	277939
26	154066	151075	142445	129160	112641	945039	762948
27	410420	402745	380592	346365	303617	256408	208656
28	109534	107561	101852	930113	819211	696042	570616
29	292519	287434	272697	249820	221013	188852	155889
30	781674	768535	730434	671138	596213	512141	425494
31	208995	205998	193732	180342	160827	138839	116041
32	559092	550288	524700	484699	433823	376242	316250
33	149637	147334	140707	130298	117018	101931	861273
34	400686	394750	377465	350340	315642	276070	234438
35	107339	105794	101294	942181	851412	747574	637832
36	287664	283643	271910	253432	229671	202396	173447
37	771245	760745	730124	681825	619552	547864	471487

TABLE II.

x .	$\sqrt{2\pi x}$.	e^x .	$\frac{e^x}{\sqrt{2\pi x}}$
21	11.4868	1318820000	114811000
22	11.7571	358491	304914
23	12.0214	974480	810624
24	12.2799	264891	215711
25	12.5331	720049	574516
26	12.7666	195730	153313
27	13.0248	532048	408488
28	13.2638	144626	109038
29	13.4986	393133	291240
30	13.7294	106865	778366
31	13.9563	290488	208141
32	14.1796	789630	556876
33	14.3995	214644	149063
34	14.6160	583462	399193
35	14.8294	158601	106951
36	15.0398	431123	286656
37	15.2472	117191	768608
38	15.4519	318559	206162
39	15.6539	865934	553175
40	15.8533	235385	148477

TABLE III.

x .	J_2^x / I_2^x .
1846721
2512121
3216506
4056694
5002660
6	-.005192
7	-.002430
8	-.000345
9000167
10000112
11000023
12	-.000005
13	-.000005
14	-.000001
15000000

TABLE IV.

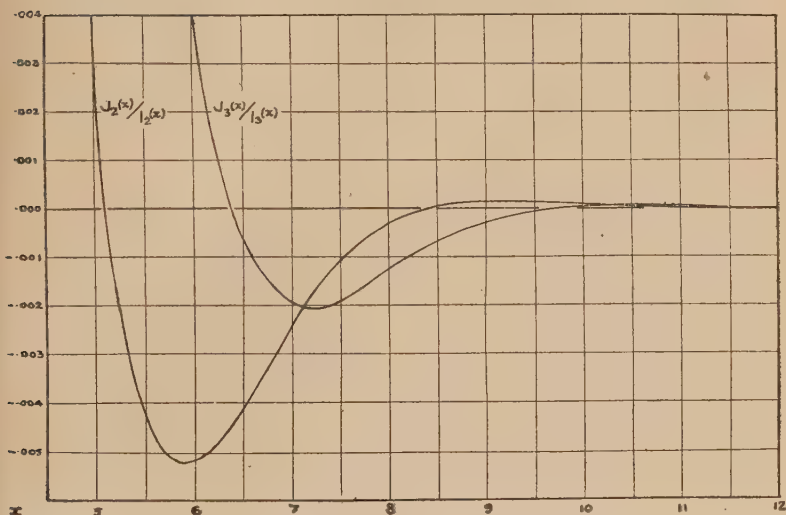
x .	$J_3(x) / I_3(x)$.
1882273
2606018
3322046
4128907
5035312
6003808
7	-.001968
8	-.001233
9	-.000280
10000033
11000048
12000015
13000000
14	-.000002
15	-.000001

The Table I. and the subsidiary Table II. are in continuation of tables given in a previous paper *. The values of $I_n(x)$ have been calculated directly from the asymptotic expansion, and the recurrence formula was used as a check. The tables are correct to five significant figures.

Tables III. and IV. give the values of the quotients

$$J_2(x)/I_2(x), \quad J_3(x)/I_3(x).$$

Fig. 1.



These quotients are of importance in certain problems in acoustics †. Graphs of these functions between the limits $x=5$ and $x=12$ are included. They have been calculated from the values of $I_n(x)$ previously given, and the values of $J_n(x)$ given in Jahnke and Emde's 'Funktionentafeln' (Leipzig and Berlin, 1909).

* Cf. Phil. Mag. xlv. pp. 846-849 (1923).

† See Proc. Roy. Soc. ci. pp. 493-508 (1922).

VI. *The Application of Oscillating Valve Circuits to the Precise Measurement of Certain Physical Quantities.* By J. E. P. WAGSTAFF, M.A., *Lecturer in Physics at the University of Leeds**.

IT has been shown by Whiddington† and others that the valve circuit can be employed very effectively to solve problems of pure Physics. In the present paper the scope of its usefulness has been extended by applying it to several quite diverse problems. Moreover, the applicability of the simple formula for the frequency of a valve circuit, $n = \frac{1}{2\pi \sqrt{LC}}$, has been fully investigated both for audible and high-frequency oscillations, and its limitations discussed.

Description of Apparatus.

The apparatus used is shown in fig. 1. V_1 and V_2 are oscillating valve circuits, the coils H, K, M, and N of which are so chosen as to produce oscillations of about a million frequency. Each pair of coils is mounted on a substantial wooden frame, and the anode and grid coils are insulated from one another by a layer of paraffin-wax paper. The variable vane condensers E and L serve to adjust the frequencies of the two circuits, and fine adjustments are effected by means of a small parallel plate condenser F in parallel with E. This is worked by means of a long ebonite arm G which projects from the box containing the condensers. The filaments of the two lamps are in parallel and are heated by means of a four-volt battery B (the negative pole of which is earthed) of as large a charging capacity as possible. It is also very important that the accumulators supplying the current to the filaments should be in excellent condition, as the success of this type of experiment depends largely on the constancy of the filament current. D is a battery of accumulators of E.M.F.=50 volts and supplies the high tension to both circuits, as shown. P is a Brown pattern loud-speaking telephone, mounted on a wooden platform above the apparatus, which emits quite a clear, constant, audible note when the circuits are working and in adjustment. No amplifier is used, as it seems best to avoid, wherever possible, all complications of the apparatus. All the wiring is of stout copper (enamel covered), and the joints

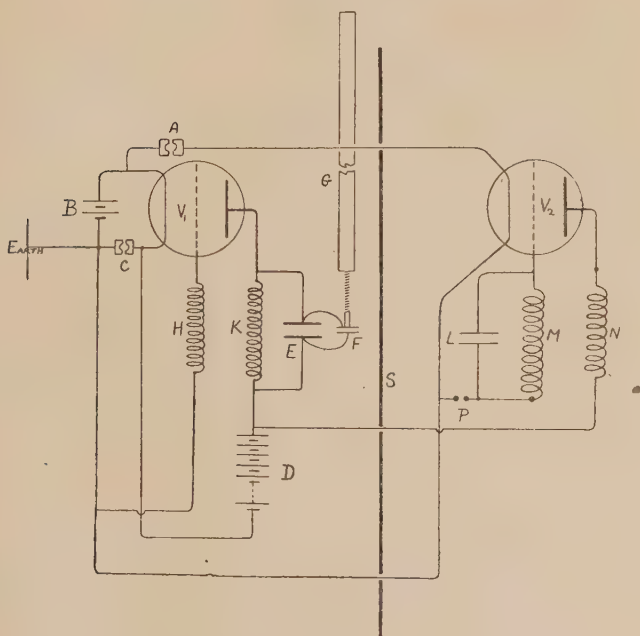
* Communicated by Prof. R. Whiddington.

† Whiddington, *Phil. Mag.* Nov. 1920.

are made as nearly perfect as possible. The apparatus is contained in four wooden cases lined with tinfoil, and covered on the outside with substantial tin sheeting, the inner and outer coatings of each box being in electrical contact and earthed. The whole is mounted on a solid stone slab. All wires passing from one box to another are protected in ebonite tubing. The two valves for maintaining the oscillations are fitted to the top of one of the boxes.

Experience has taught me that it is only when conditions are very quiet that the apparatus works satisfactorily. A

Fig. 1.



footfall overhead, the slamming of a door in a distant part of the building, is sufficient to produce a small change (usually one or two beats per sec.) in the frequency of oscillation. Consequently it has been necessary to do most of the work described in this paper between the hours of midnight and 3 A.M., when conditions are as nearly perfect as possible. When proper conditions are obtained the beats are remarkably steady; there is always a tendency for a slight variation, and this I attribute, as a result of a long and careful investigation, to variations in

the battery B. The kind of steadiness obtained is given in the following table, where the time of 50 beats is tabulated against the interval between observations:—

TABLE I.

Interval between observations.	Time for 50 beats.
0	18.5 sec.
1 min. later	18.0 "
2 "	17.5 "
3 "	17.2 "
5 "	16.6 "
6 "	16.5 "
7 "	16.0 "
8 "	16.0 "
9 "	16.0 "

In order to provide an unvarying standard of pitch to which the note can be adjusted, another valve circuit V is set up with capacities and inductances so large as to produce an audible note in the telephone placed in the anode circuit. A separate filament battery and high-tension battery are used for this circuit. The capacity consists of a standard condenser box having a range of capacities from .001 m.f. to 1 m.f.

Standardization of the Oscillating Circuits.

When the circuits had been constructed as indicated in the last paragraph, and beats of steady frequency could be heard when the three circuits were oscillating, the various parts were accurately calibrated.

Calibration of the Oscillating Circuit of Audible Frequency.

For this experiment a set of standard tuning-forks was employed. The note emitted by the audible circuit was altered by accurately adjusting the capacity in the standard condenser, keeping everything else in the circuit constant, until resonance was obtained between the circuit and a given fork (*i.e.*, until no beats could be detected). With the higher notes ($n=1024$, $n=1536$, etc.) the experiment was slightly modified by adjusting the capacity in the box until the audible note was an octave of the fork. In the neighbourhood of the correct capacity beats became quite audible. It was rather difficult to decide at times with the ear, owing to the difference in quality of the two notes, which octave of the fork was being emitted. This was easily settled, however, by counting the number of beats

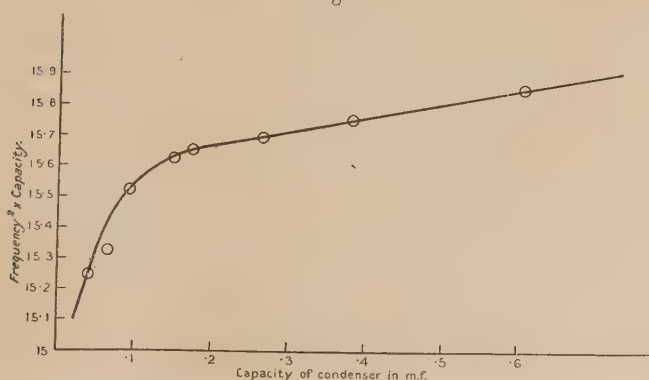
produced per second between the fork and the circuit, corresponding to a small change in the capacity of the latter. In the table below is shown the capacity in the box for various frequencies of note emitted. The numbers have been checked from time to time and have shown no material variation over a period of eight months.

TABLE II.

Frequency of note.	Capacity in box. m.f.	$n^2C \times 10^{-4}$.	$\cdot 26C - \frac{0.022}{C}$.	$n^2(C+c) \times 10^{-4}$.
512	·605	15·86	+·12	15·92
643	·381	15·76	+·04	15·82
768	·266	15·70	-·0135	15·80
955	·172	15·66	-·04	15·85
1024	·149	15·63	-·109	15·81
1286	·094	15·53	-·21	15·85
1536	·065	15·33	-·3216	15·76
1929	·041	15·25	-·526	15·92

It is seen that n^2C is not constant, but tends to decrease as the frequency increases. In fig. 2 columns 1 and 3 have been plotted.

Fig. 2.



The relationship between n^2C and C is represented by the equation

$$n^2C = 10^4 \left(15.74 + 0.26C - \frac{0.022}{C} \right).$$

This is best seen by plotting n^2C against $\left(\cdot 26C - \frac{0.022}{C} \right) 10^4$.

The corresponding values of the two variables for different values of C are given in columns 3 and 4 of Table II. A straight-line relationship, which is of course purely empirical, is indicated between the variables. Incidentally the term 15.74×10^4 , which is independent of C , can be used to find the self-induction of the anode coil. It is the constant in the expression, and can be identified with

$\frac{1}{4\pi^2 L}$. It has been found possible to interpret the results differently. The quantity C , up to now, only takes into account the capacity of the oscillating circuit introduced by the condenser, and this is calibrated for static fields. If a capacity $\bar{c} = .0018$ m.f. be added to C , $n^2(C + \bar{c})$ is seen to be constant to an accuracy of 1 per cent. over the range of frequencies used. Hence for an audible circuit of constant self-induction, $n^2 C$ is constant in accordance with the law $n = \frac{1}{2\pi \sqrt{LC}}$, provided a sufficiently broad interpretation of C is taken.

Standardization of the High-frequency Circuit.

Having justified the assumption that the frequency in the case of audible circuits is represented within 1 per cent. by a formula of the form $n^2(C + c) = \text{constant}$, I directed my attention to the corresponding problem in the case of the valve circuit of high-frequency oscillations. The condenser used in this circuit was of the variable vane type, and this was first calibrated with a ballistic galvanometer so that the absolute capacity was known corresponding to any position of the vanes. The procedure was that usually adopted in this type of problem, the condenser being charged up by connecting its terminals to the pole of a battery of E.M.F. = 200 volts, and subsequently discharged through a suitable galvanometer.

The results were standardized by discharging through the galvanometer condensers of known capacity. The relationship between the capacity and the scale-reading was found to be linear and of the form

$$C_{\text{m.f.}} = 10^{-5}(87.04 - .3758x),$$

where x is the scale-reading.

At this stage, keeping everything else constant (*e. g.* battery potentials, inductances, etc.), the wave-lengths of the oscillations generated in the circuit were measured by a standard wave-meter for various values of the capacity, and the results afterwards confirmed with a Fleming cymometer. The results are tabulated here.

TABLE III.

Scale-reading.	Capacity C. m.f.	Wave-length λ . cm.	Frequency = $\frac{c}{\lambda}$.	Frequency ² .	Frequency ² \times C.	Frequency ² (C + c).
174	21.67×10^{-5}	2.139×10^5	1.492×10^5	2.226×10^{10}	48.25×10^5	107.98×10^5
140	34.44×10^{-5}	2.255×10^5	1.330×10^5	1.769×10^{10}	60.94×10^5	108.4×10^5
120	41.95×10^{-5}	2.414×10^5	1.243×10^5	1.545×10^{10}	64.79×10^5	106.24×10^5
100	49.46×10^{-5}	2.555×10^5	1.174×10^5	1.378×10^{10}	68.17×10^5	105.15×10^5
80	56.98×10^{-5}	2.681×10^5	1.119×10^5	1.251×10^{10}	71.31×10^5	105.15×10^5
60	64.49×10^{-5}	2.801×10^5	1.071×10^5	1.148×10^{10}	73.98×10^5	104.87×10^5
40	72.01×10^{-5}	2.877×10^5	1.043×10^5	1.087×10^{10}	78.3×10^5	107.49×10^5
20	79.524×10^{-5}	2.977×10^5	1.008×10^5	1.015×10^{10}	80.74×10^5	107.98×10^5

It will be noticed that n^2C is here not even approximately constant, so that either $n = \frac{1}{2\pi\sqrt{LC}}$ can no longer be applied or a much broader interpretation of C is necessary. n^2C can be shown to be related to C by an empirical equation of the form

$$n^2C = 61.411 \times 10^5 + \left(.3133 \times 10^{10}C - \frac{432.5}{C} \right).$$

The similarity in the relationships between frequency and capacity for low-frequency and high-frequency circuits is in this way strikingly demonstrated. In each case a simple equation of the form

$$n^2C = A + BC + \frac{D}{C}$$

suffices to represent the relationship. An attempt was again made to interpret the results on the lines indicated in the last section. Assuming, as the results up to now indicate, that the relationship between frequency and capacity for high-frequency oscillations does not differ fundamentally from that deduced for low-frequency oscillations, it is justifiable to write

$$n^2(C + \bar{c}) = \text{constant}.$$

Taking the first and last values of n and C in the above table, the equation becomes

$$48.25 \times 10^5 + 2.226 \times 10^{10}\bar{c} = 80.74 \times 10^5 + 1.015 \times 10^{10}\bar{c}.$$

$$\bar{c} = 26.83 \times 10^{-5} \text{ m.f.}$$

This is the additional capacity to be added to C .

If this additional capacity \bar{c} remains approximately constant for the range of wave-lengths used,

$$n^2(C + 26.83 \times 10^{-5}) = \text{constant}.$$

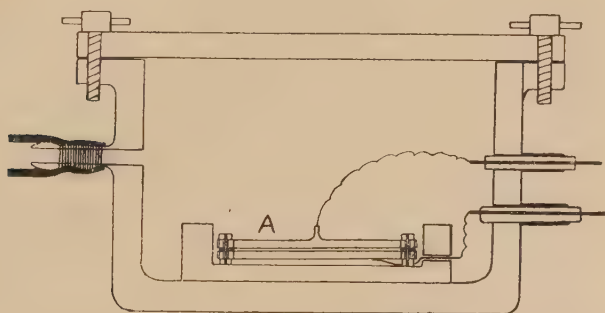
In the last column of the above table is calculated $n^2(C + 26.83 \times 10^{-5})$ for the values of C given in column 2.

The values are constant to within 3 per cent., and this variation can probably be further reduced by choosing a more judicious value for \bar{c} . Thus it follows that for low- and high-frequency circuits, $n^2(C + \bar{c})$ is reasonably constant, where c is a suitably chosen capacity for each circuit used.

*Determination of the Dielectric Constant of Air and
its Variation with Pressure.*

The first series of experiments undertaken with the above apparatus was the determination of the dielectric constant of air and its variation with pressure. The condenser (fig. 3) used in this investigation consisting of two steel plates 4 in. \times 3 in. \times $\frac{1}{4}$ in., separated by circular plugs of ebonite 1 mm. thick, was placed in parallel with the variable vane condenser E. The plates were clamped together by means of screw pins and small nuts as shown. The pins were insulated from the condenser plates by passing them through ebonite plugs inlaid in the plates, concentric with those separating the plates and very slightly smaller than the latter in diameter, and the nuts were screwed down on these.

Fig. 3.



The condenser rested in an ebonite cradle to insulate it from the wall of the pressure chamber, which was earthed. The pressure chamber consisted of a very strong brass casting, with $\frac{3}{4}$ in. walls, connected to the exhaust pump through the side tube by pressure tubing. Thick brass wires, fitted in fibre plugs and passing through the side of the vessel as shown, served as leads to the condenser. To ensure that any slight contraction of the chamber produced no strain on the condenser plates, the leads were joined to the plates by two small coils of very fine, insulated, copper wire.

Precautions of the kind just described are essential in experiments with valve circuits, otherwise the effects to be measured are completely masked by spurious effects arising from such causes as change in the size or shape of the pressure chamber, or in the disposition of the condenser plates inside the chamber.

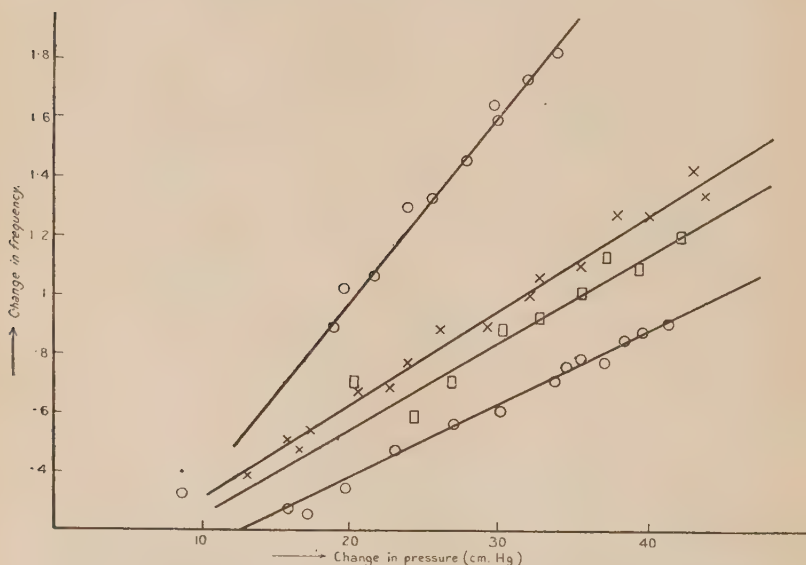
The top of the casting was secured to the body by

thumb-screws, and a piece of indiarubber placed between the two was found very useful in rendering the apparatus air-tight. An ordinary mercury manometer served to register the pressure inside the chamber.

Method of procedure.

The valve circuits V , V_1 , and V_2 were made to oscillate, and the capacities were adjusted until slow beats at the rate of about 2 per second could be heard in the telephones. The vessel was now partially exhausted, and when conditions were steady again the time for 50 or 100 beats was

Fig. 4.



measured with a stop-watch. The pressure was immediately released, and the time of 100 beats again measured. Various initial pressures varying from 10 to 40 cm. were used, and the series was repeated for various frequencies of oscillation. In this way the change of frequency of the circuit V_1 was measured for a given change of pressure inside the chamber. Fig. 4 shows the "change in pressure" plotted against "corresponding change in frequency" for all the frequencies used, and it is evident that the change in frequency is a linear function of the change in pressure.

In order to calculate the dielectric constant of air from the observations the capacity of the condenser had still to

be determined. This was done with a heterodyne beat method, by finding the change in the frequency of the audible circuit, when the parallel plate condenser and its earthed case were connected in parallel with the standard condenser. The determination was repeated for several frequencies of the circuit, and very good agreement was obtained.

That the method is capable of giving reliable results was confirmed by substituting for the condenser A a condenser of known and calculable capacity. Excellent agreement was obtained with the calculated value and with the value determined by electrostatic methods.

We are now in a position to calculate the dielectric constant of air.

The frequency of an oscillating circuit is given by the equation

$$n = \frac{1}{2\pi\sqrt{LC}},$$

where C is the *total* capacity of the circuit, and L is the coefficient of self-induction of the anode circuit.

Corresponding to a change in capacity dC , the frequency is

$$n - dn = \frac{1}{2\pi\sqrt{L(C + dC)}},$$

therefore
$$\left(\frac{n}{n - dn}\right)^2 = \frac{C + dC}{C},$$

i. e.
$$\frac{2dn}{n} = \frac{dC}{C}.$$

If c_1 is the capacity of the parallel plate condenser A (fig. 3), and the change in capacity dC is due to the withdrawal or admission of air into the chamber containing A,

$$dC = c_1(K - 1)\frac{p_1}{\Pi},$$

where p_1 is the change of pressure in the chamber, and Π is the atmospheric pressure.

Therefore
$$K - 1 = \frac{2\Pi}{n} \cdot \frac{C}{c_1} \cdot \frac{dn}{p_1}.$$

For a particular value of n , $\frac{dn}{p_1}$ is given by the slope of the appropriate line in fig. 4.

The values of $K-1$ for the values of C employed are shown in the following table :—

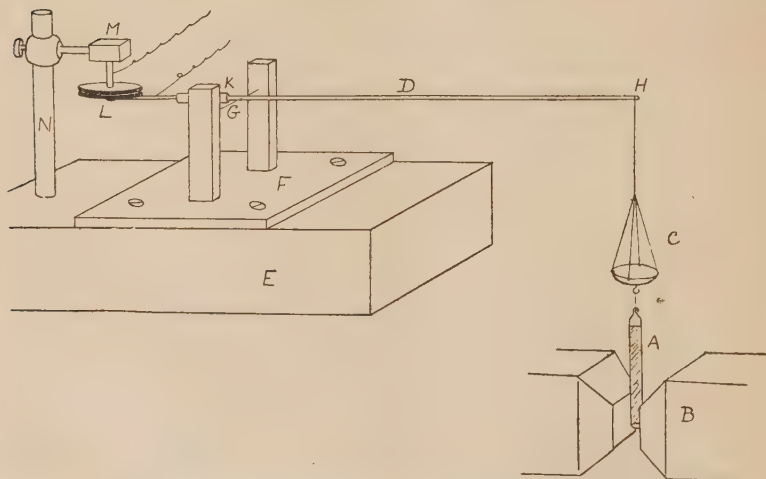
TABLE IV.

c_1 (mean value of 27 observations) = 5.50×10^{-5} m.f.

Scale-reading.	Capacity of vane condenser.	Total capacity C .	Frequency of oscillations.	$K-1$.
40	72.01×10^{-5} m.f.	104.34×10^{-5} m.f.	1.015×10^5	.0006817
80	56.98×10^{-5} m.f.	89.31×10^{-5} m.f.	1.083×10^5	.0006612
120	41.95×10^{-5} m.f.	74.28×10^{-5} m.f.	1.196×10^5	.0005976
174	21.67×10^{-5} m.f.	54.00×10^{-5} m.f.	1.415×10^5	.0006639

The values obtained for $K-1$ are in good agreement with those obtained by other investigators. These results therefore confirm the hypotheses made earlier in the paper.

Fig. 5.



Application of the Oscillating Valve Circuit to the Determination of Magnetic Susceptibilities for Steady Fields.

The arrangements used for applying this method to the measurement of magnetic susceptibility in steady fields are shown in fig. 5. The upper plate of an air condenser L

is clamped to a vertical upright N fixed rigidly to a steel base E which is earthed. An ebonite plug M serves to insulate the plate. The lower plate is fastened to a long brass rod D (being insulated from it by the ebonite plug K), and is suspended between two stout vertical uprights F by means of a thin horizontal steel wire G about 3 in. long. This wire, which is soldered to the brass rod D, is drawn through the two vertical uprights under tension and fastened securely to them. Thus the lower plate of the condenser and the rod can move in a vertical plane, and the motion is controlled by the torsion of the wire G. This apparatus is contained in an earthed case, with the arm D projecting. The specimen A to be examined is suspended from H so as to lie symmetrically between the poles of an electromagnet B. For purposes of calibration it has been found convenient to include a scale-pan C in the suspended system.

Before commencing the experiment, by means of sliding weights fixed to the arm D, the lower plate of the condenser is adjusted so as to lie horizontal when free, and the upper plate is clamped at a vertical distance of 1 mm. above it. The arrangement replaces the condensers E and F in fig. 1. The current to the electromagnet is obtained from a large battery of accumulators, and the circuit includes an ammeter, rheostat, and plug. A commutator is also arranged in the circuit for reversing the current through the coils of the electromagnet.

Theory.

The above apparatus is essentially a delicate torsion-balance, which is capable of measuring small changes in the tension applied at H. In the experiments to be described, it has been found comparatively simple by this method to measure $\frac{1}{4}$ dyne, but $\frac{1}{100}$ part of this amount can also be estimated. It can be proved that if a specimen of cross-section A and susceptibility μ is suspended in a horizontal magnetic field of varying intensity, there is a pull P vertically downwards on the specimen, where

$$P = \frac{\mu A}{2} (H_0^2 - H_1^2) *,$$

H_0 and H_1 being the strengths of the magnetic field at the two ends. For a long rod $H_1 = 0$, and the expression for P reduces to

$$P = \frac{\mu H_0^2 A}{2}.$$

* Maxwell, 'Electricity and Magnetism,' 3rd ed. vol. ii. p. 74.

Thus by switching on the current through the electromagnet, the pull applied to H is altered by a definite amount. This produces a small change in the distance between the two plates of the condenser L, and if the circuit V_1 is oscillating, a slight change occurs in the frequency of oscillation. This can be measured by means of the auxiliary circuits V_2 and V.

Method of experiment.

When the torsion-balance was fitted up as explained above, and the specimen suspended symmetrically between the pole-pieces of the electromagnet, the valve circuits V_1 , V_2 , and V were set oscillating and the capacities adjusted until slow beats could be heard. The time for 50 beats was measured with a stop-watch, the current through the electromagnet switched on, and the time for 50 beats again measured, the current registered by the ammeter being carefully noted. When the field was switched off, a third measurement of the frequency of the beats was made and any slight change due to drift eliminated.

The results obtained for a rod of bismuth are given below :—

Diameter of section of rod = .643 cm.

Current in electromagnet = 5 amp.

Capacity in audible circuit = .157 m.f.

Change in frequency of V_1 when current through the electromagnet is switched on = 5.486 oscill./sec.

The above change in frequency is the mean value of 29 observations, which show extreme variations of ± 0.1 about the mean. In order to interpret these readings, definite loads were added to the scale-pan C, and the change in frequency of the circuit V_1 determined. It was also noticeable that whereas the addition of weights made the beats faster, switching on the field made them slower. This corresponds to a negative coefficient of susceptibility in the case of bismuth.

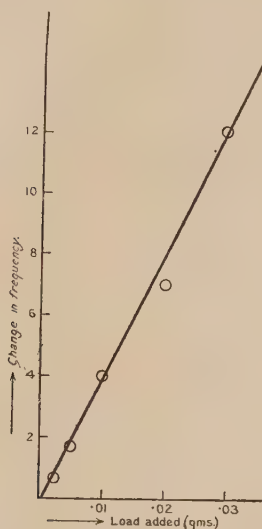
TABLE V.

Mass added to scale-pan.	Change in frequency of V_1 .
.002 gm.663
.005 „	1.715
.01 „	4
.02 „	7
.03 „	12

In fig. 6 the values recorded in the above table are plotted, and it is obvious that for small loads a linear relationship exists between the change in frequency of V_1 and the load added to the scale-pan. From the curve, the load corresponding to a change in frequency of 5.486 is found to be .0137 gm.

The experiment with bismuth was repeated, with the plates of the condenser L so close together that quite an appreciable change of note occurred when the current through the electromagnet was switched on. In this case

Fig. 6.



the change in frequency of V_1 was estimated by altering the capacity of the audible circuit V until resonance was again obtained, and calculating from the constants of that circuit the change in frequency corresponding to the given change in capacity. The results are given below :—

Current through electromagnet = 5 amp.

Mean change in frequency of V_1 when current through electromagnet is switched on = 72, with an extreme variation for 6 observations of ± 4 about the mean.

The readings were again standardized by adding known weights to the scale-pan, and finding the corresponding change in frequency of the note emitted by the circuit.

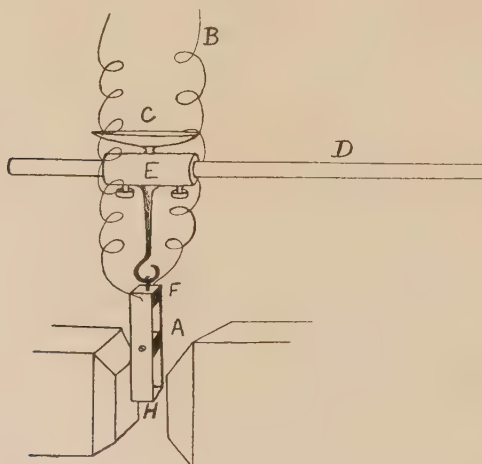
The alteration in load corresponding to a change in frequency of 72 was found to be .0128 gm. wt.

Determination of the Strength of the Magnetic Field between the Poles of the Electromagnet.

Before the magnetic susceptibility could be calculated, it was necessary to find the value of H_0 —the magnetic field between the pole-pieces. This was done by two independent methods, and the results were compared.

In the first method a small test coil was wound on a flat plate of ebonite $\frac{1}{2}$ cm. long, .6835 cm. wide, and .162 cm. thick with enamel-covered wire of the finest gauge. This coil was arranged in series with a ballistic galvanometer and the secondary of a standardizing coil, and placed midway between the poles of the electromagnet so that the turns of the coil cut the lines of the field at right angles. The throw obtained when the current through the electromagnet was reversed was compared with that obtained when a suitable current through the primary of the standardizing coil was similarly reversed. As a result of several observations, H_0 was found to be 2414 gauss.

Fig. 7.



In order to confirm the above value of H_0 , a second determination was made by finding the force on a current circuit placed in the position H between the pole-pieces of the electromagnet. The arrangement used is shown in fig. 7. The frame A consists of two parallel vertical copper strips 3 in. long, $\frac{1}{3}$ in. wide, and $\frac{1}{3}\frac{1}{2}$ in. thick, to the bottom of which is soldered a horizontal cross-piece of copper, of rectangular section and of the same area approximately as the

bismuth rod. Small pieces of ebonite screwed to the strip at F and F' serve to keep them quite parallel. This frame is hooked to a sliding-piece E, which can be fixed anywhere along the arm D, and which supports the scale-pan G. The current to A is conveyed through two spiral coils of extremely fine copper wire B. The circuit containing A includes a reversing commutator, a reliable milliammeter, resistance-box, key, and a 2-volt battery.

Method of experiment.

The suspended frame was first of all adjusted so that the current through the horizontal cross-piece flowed perpendicular to the lines of the magnetic field. The circuits were made to oscillate as before, the capacity in the audible circuit being adjusted until extremely slow beats (one in two seconds) could be heard between the circuits. A current was sent through the frame and the capacity altered until beats of the same frequency were again audible. Then, from the known constants of the audible circuit, the change in frequency of V_1 was immediately determined :

Current through cross-piece = .038 amp.

Length of conductor = .734 cm.

Mean change in frequency of V_1 on switching on current through electromagnet = 24.46.

The readings were again calibrated by adding known weights to the pan and observing the corresponding change of frequency, and it was found that a change of frequency of 24.46 corresponded to an additional pull of .00695 gm. wt. Now, if a conductor of length l cm., carrying a current i e.m.u., is situated in a field of intensity H_0 , there is a mechanical force on the conductor perpendicular to the plane of i and H_0 and of magnitude P given by

$$P = ilH_0.$$

It is obvious that the vertical sides of the frame give no contribution to the resultant force downwards.

$$\text{Hence, since } i = \frac{.038}{10} \text{ e.m.u.,}$$

$$l = .734 \text{ cm.,}$$

$$P = .00695 \times 981 \text{ dynes,}$$

$$\text{and } H_0 = 2444 \text{ gauss,}$$

which agrees with the previous determination to an accuracy of about 1 per cent.

The susceptibility of bismuth can now be calculated from the formula $\mu = \frac{2P}{AH_0^2}$:

The first series of experiments gives $\mu = -13.86 \times 10^{-6}$,

The second „ „ „ $\mu = -12.94 \times 10^{-6}$,

for which the mean value is -13.4×10^{-6} , and this is in very close agreement with the best values previously obtained.

The magnetic liquid Nickel Carbonyl was next investigated by this method. Although the susceptibility of this liquid is of a much lower order than that of bismuth, the method has given consistent results for μ . The liquid was contained in a tube and suspended from the arm D as before. The operations were carried out in exactly the same way as described in the previous experiment. Owing to the small susceptibility of the liquid, changes of frequency had to be estimated by the beat method throughout. The results of the two series of observations taken are given below:—

SERIES I.

Mean diameter of tube = .6781 mm.

Current through electromagnet = 5 amp.

Mean change of frequency = -1.400 , which corresponds to a change in tension of $-.00037$ gm. wt. The negative sign indicates that the liquid is diamagnetic.

SERIES II.

Mean diameter of tube = .9467 mm.

Current through electromagnet = 5 amp.

Mean change of frequency = $-.1979$, which corresponds to a change in pull on the arm D of $-.00063$ gm. wt.

From Series I.

the susceptibility of nickel carbonyl = $-.34 \times 10^{-6}$,
and from Series II.

the susceptibility of nickel carbonyl = $-.30 \times 10^{-6}$.

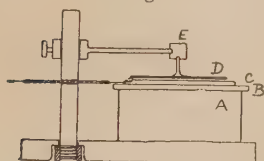
The method is thus capable of measuring low order susceptibilities.

In the above, calibration experiments were carried out for each set of observations taken. This is not at all necessary, generally, but for the preliminary set of experiments it was thought desirable to perform them under widely varying conditions so as to test the kind of accuracy that was to be expected.

Experiments to investigate the Effect of Electrostatic Charge on the Surface Tension of a Mercury-Air Surface.

Recently I became interested in the question of the effect on its surface tension of charging up a mercury surface, and devised an experiment to demonstrate its existence or otherwise. The oscillating valve circuits of the previous sections were again utilized in a manner shown in fig. 8.

Fig. 8.



A large drop of mercury C was placed on a plate of perfectly clean glass B, which rested on a steel slab A, fixed to a strong stand. Electrical contact with the drop was maintained by means of a thin platinum wire, fused into a glass tube filled with mercury, which just pierced the surface of the drop. A metal plate D was fixed above the upper surface of the drop by clamping it to the same stand. An ebonite plug E served to insulate D from the stand. The distance between C and D was adjusted to be about $\frac{1}{5}$ mm. by a fine screw fixed to D, unfortunately omitted from the drawing. C and D being only $\frac{1}{5}$ mm. apart, it was very difficult at times to keep them separate; the slightest vibration brought the mercury into contact with the plate, and the various adjustments had then to be repeated. In one series, to prevent this, a very thin glass cover-slip was made to rest on the surface of the mercury, and this was found to overcome the difficulty completely. The above arrangement constituted a parallel plate condenser, of which D formed one plate and the mercury drop the other, and was substituted for E and F (fig. 1). The potential of the battery D was reduced as much as possible, and the earthed wire at C was removed.

Theory.

Since the condenser formed by D and the mercury constitutes most of the capacity in the circuit V_1 , any change in the distance CD will profoundly modify the frequency of oscillation of that circuit. This distance will be changed if, due to any cause, the thickness of the drop is made to change, and any alteration in the surface tension of the mercury will effect this. It has been estimated that a change in the thickness of the drop of 10^{-6} can be detected.

Method of experiment.

The circuits V_1 , V_2 , and V were made to oscillate, and the capacities adjusted until slow beats (2 or 3 per second) could be heard. The mercury drop was earthed and the frequency of the beats counted. The earth was now removed, and the bubble placed in electrical contact with the positive pole of a battery of E.M.F.=200 volts, the negative pole of which was earthed, and the frequency of the beats again measured.

No change whatever could be detected.

Hence it must be concluded that no variation in the surface tension of the mercury resulted when the drop was charged to a potential of 200 volts.

In conclusion, I wish to express my thanks to Professor R. Whiddington for his interest in the work and for his helpful suggestions, and to the Grants Committee of the Royal Society who helped to defray the cost of the apparatus.

University of Leeds,
August 8th, 1923.

VII. *The Characteristic Vibration Frequency of an Element.*

By J. E. P. WAGSTAFF, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics at the University of Leeds*.

FROM considerations of the distribution of atoms in a substance and the forces acting on them when they are displaced from their positions of equilibrium, Einstein † has shown that the characteristic frequency ν of the body can be determined in terms of the compressibility κ , the atomic volume V , and the atomic weight M by means of the formula

$$\nu = \beta \frac{V^{1/6}}{\kappa^{1/2} M^{1/2}}, \quad \dots \dots \dots (I.)$$

where $\beta = 2.54 \times 10^7$.

Speculations on certain results I have been obtaining have led me to investigate the amount and nature of the variation that occurs in the quantity β (theoretically a constant) in the above formula as one passes from element to element, and the results seem of sufficient interest to

* Communicated by the Author.

† Einstein, *Annalen der Physik*, xxxiv. p. 170 (1911).

publish. Incidentally, an instructive method of deriving (I.) has been evolved and is included in the paper.

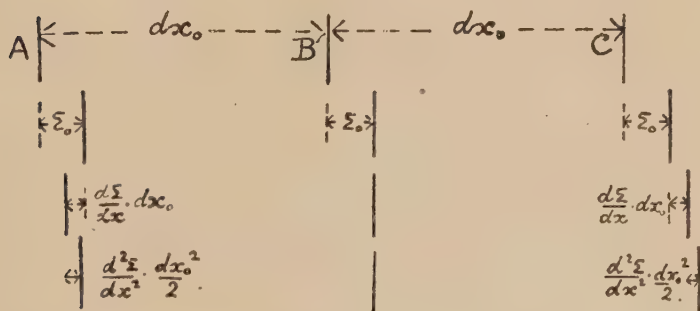
Suppose the substance contains atomic vibrators of frequency ν , then according to the simple theory of harmonic motion,

$$\frac{1}{\nu} = 2\pi \sqrt{\frac{m}{f}},$$

where m is the atomic mass, and f is the restoring force corresponding to unit displacement from the equilibrium position, which is in all probability a position of symmetry with respect to adjacent layers. If one supposes the substance to be built up of small cubes of sides dx_0 , each cube containing one atom, dx_0 represents the initial distance between the successive layers.

Consider three such layers represented by the planes A, B, C (fig. 1), and suppose B is displaced an amount Σ_0 .

Fig. 1.



The displacement of C is

$$\Sigma_C = \Sigma_0 + \frac{d\Sigma}{dx} \cdot dx_0 + \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2} + \dots$$

and the displacement of A is

$$\Sigma_A = \Sigma_0 - \frac{d\Sigma}{dx} \cdot dx_0 + \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2} + \dots$$

The plane B is thus displaced from its position of symmetry with respect to the two adjacent planes by an amount $\frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2}$, and is therefore subjected to a force of magnitude $f \frac{d^2\Sigma}{dx^2} \cdot \frac{dx_0^2}{2}$ acting in the direction BC.

If the longitudinal stress at A is $\frac{P}{a}$, we can write

$$\frac{f}{2} \cdot \frac{d^2 \Sigma}{dx^2} \cdot dx_0^2 = \frac{dP}{dx} \cdot dx_0 \frac{dx_0^2}{a},$$

where a is the cross-section of the material.

$$\begin{aligned} \therefore P &= a \cdot \frac{f}{2 dx_0} \cdot \frac{d \Sigma}{dx}, \\ &= a \cdot \frac{2 \pi^2 \nu^2 m}{dx_0} \cdot \frac{d \Sigma}{dx}. \end{aligned}$$

But in the case of a simple elongation of the material (lateral forces being applied so that no change in the lateral dimensions occurs in spite of the longitudinal tension), the longitudinal component of the stress is related to the strain by the equation

$$\frac{P}{a} = j \cdot \frac{d \Sigma}{dx},$$

$$\text{where } j = \frac{3(1-\sigma)}{\kappa(1+\sigma)},$$

κ being the compressibility and σ Poisson's ratio.

$$\begin{aligned} \therefore \frac{2 \pi^2 m \nu^2}{dx_0} &= j = \frac{3(1-\sigma)}{\kappa(1+\sigma)}, \\ \therefore \nu &= \frac{1}{\pi} \left\{ \frac{3 dx_0 (1-\sigma)}{2 m \kappa (1+\sigma)} \right\}^{1/2}. \quad \text{(II.)} \end{aligned}$$

Suppose M is the atomic weight of the element, V the atomic volume, and ρ the density.

$$\text{Then } m = M \times 1.64 \times 10^{-24},$$

$$\text{and } \frac{m}{dx_0^3} = \rho = \frac{M}{V}.$$

Substituting for m and dx_0 in (II.),

$$\nu = 3.306 \times 10^7 \frac{V^{1/6}}{M^{1/2} \kappa^{1/2}} \left(\frac{1-\sigma}{1+\sigma} \right)^{1/2}, \quad \text{(III.)}$$

which reduces for $\sigma = \frac{1}{4}$, to

$$\nu = 2.56 \times 10^7 \frac{V^{1/6}}{M^{1/2} \kappa^{1/2}}$$

which is Einstein's formula.

In the following table the values of ν (derived from (III.)) for several elements are tabulated.

TABLE I.

Element.	σ .	Atomic Weight.	ν (From III.)	ν (From I.)	ν (Lindemann's melting-point method.)	ν (observed).
Copper	26	63.6	6.0×10^{12}	5.7×10^{12}	6.7×10^{12}	6.6×10^{12}
Lead	446	207	1.55	2.2	1.84	1.9
Aluminium ..	31	27.1	5.93	6.6	7.5	8.3
"	16	"	7.0	"	"	"
Mercury.....	0	200	1.9	1.46	1.3	2.2
Iron	28	55.9	7.3	6.5	8.3	—
Bismuth	33	208	1.6	1.8	1.6	—
Cadmium	3	112	2.6	2.6	3.0	—
Gold	422	197	3.23	3.8	3.4	—
Nickel	31	58.7	8.27	6.6	8.2	—
Palladium	39	107	5.0	5.8	5.74	—
Platinum	39	195	5.0	4.6	4.36	—
Tin	33	119	2.6	2.8	2.24	—
Zinc	21	65.4	3.9	3.73	4.36	4.8×10^{12}

From the above table, it is seen that the values obtained for ν are in moderately good agreement with those given by Einstein and Lindemann.

Consider now the mean energy of an atomic vibrator of frequency ν and amplitude γ , whose motion is represented by an equation of the form $\Sigma = \gamma \sin 2\pi\nu t$. The energy associated with such a vibration $= 2m\pi^2\nu^2\gamma^2$, so that the energy associated with the vibration of atoms in a layer of thickness dx_0 and area a , containing N vibrators per unit volume $= 2m\pi^2\nu^2\gamma^2Na dx_0$.

The work necessary to produce elastic oscillations of the same amplitude

$$= \frac{dP}{2} \cdot \gamma,$$

$$\text{where } dP = 2aj \frac{\gamma}{dx_0},$$

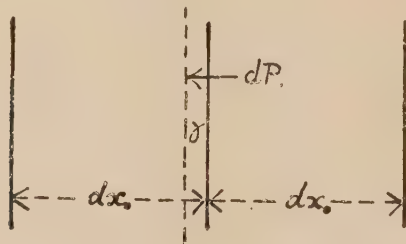
from the simple theory of stress and strain, j being the appropriate modulus of elasticity (fig. 2).

$$\begin{aligned}
 & \therefore \frac{\text{Energy associated with atomic vibrations of amplitude } \gamma}{\text{Work necessary to produce elastic oscillations of same amplitude}} \\
 &= \frac{\text{Energy associated with atomic vibrations of amplitude } \gamma}{\text{Energy associated with elastic vibrations of same amplitude}} \\
 &= \frac{2m\pi^2\nu^2 N dx_0^2}{j} \\
 &= \frac{2\rho\pi^2\nu^2\kappa(1+\sigma)V^{2/3} \times (1.64)^{2/3} \times 10^{-16}}{3(1-\sigma)} = 1,
 \end{aligned}$$

on substituting for $\nu^2\kappa \frac{V^{2/3}(1+\sigma)}{(1-\sigma)}$ from equation (III.), *i. e.*,

bodies for which the Einstein law holds are those whose atomic energy can be ascribed to the state of strain of the body.

Fig. 2.



As a further step we might suppose the quantity $\rho\kappa\nu^2V^{2/3}$ is a measure of the ratio

$$\frac{\text{Energy associated with free atomic vibrations}}{\text{Energy associated with elastic vibrations}}$$

and that elements with values of $(\rho\kappa\nu^2V^{2/3})^{1/2}$ large compared with 2.54×10^7 are those whose atomic energy is in excess of that accounted for as strain energy.

In Table II. values of $(\rho\kappa\nu^2V^{2/3})^{1/2}$ have been tabulated for a large number of elements. The values of κ given are according to Richards*, while the values of V are due to Stefan Meyer†. The atomic frequencies have in general been calculated from Lindemann's melting-point formula, though, where known, observed values have been used instead.

In fig. 3, the quantity $(\rho\kappa\nu^2V^{2/3})^{1/2}$ has been plotted against the atomic number of the element, and the observations joined

* Richards and Stull, *Zeitschrift für Phys. Chemie*, lxi. p. 183 (1908).

† Elster and Geitel-Festschrift, Braunschweig, p. 152 (1915).

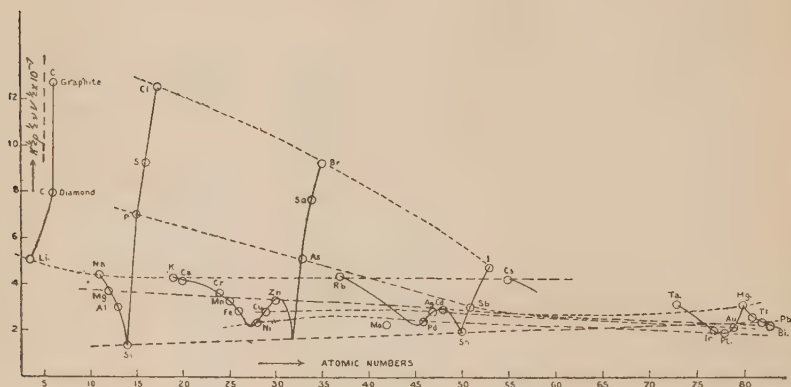
TABLE II.

Element.	Atomic Volume.	$\nu \times 10^{-12}$.	κ .	ρ .	$\kappa^{\frac{1}{3}} \nu V^{\frac{1}{3}} \rho^{\frac{1}{2}}$.
Lithium.....	13.0	10.0	8.8×10^{-12}	0.534	5.097×10^7
Carbon Diamond	3.42	40.0	0.5	3.52	7.997
„ Graphite.	5.4	27.7	3.0	2.3	12.76
Sodium.....	23.7	3.96	15.4	0.98	4.42
Magnesium.....	13.4	7.2	2.7	1.74	3.706
Aluminium.....	10.0	7.5	1.3	2.6	3.03
Silicon.....	11.4	9.6	0.16	2.48	1.36
Phosphorus, Red.	14.4	6.3	9.0	2.34	7.03
Sulphur.....	15.5	7.3	12.5	2.07	9.26
Chlorine.....	25.0	3.68	95.0	1.42	12.5
Potassium.....	45.5	2.3	31.5	0.87	4.3
Calcium.....	25.9	4.9	5.4	1.53	4.17
Chromium.....	7.76	8.3	0.7	6.9	3.61
Manganese.....	7.43	7.5	0.67	7.37	3.25
Iron.....	7.1	8.3	0.4	7.85	2.83
Nickel.....	6.67	8.2	0.27	8.8	2.37
Copper.....	7.10	6.7	0.54	8.9	2.83
Zinc.....	9.5	4.8	1.5	7.13	3.32
Arsenic.....	13.3	4.36	4.3	5.64	5.13
Selenium.....	18.5	4.06	11.8	4.3	7.64
Bromine.....	25.1	2.45	51.8	3.19	9.22
Rubidium.....	56.2	1.45	40.0	1.52	4.33
Molybdenum.....	11.1	6.7	0.26	8.65	2.24
Palladium.....	9.3	5.46	0.38	11.4	2.39
Silver.....	10.3	4.36	0.84	10.5	2.82
Cadmium.....	13.6	3.0	1.9	8.6	2.895
Tin.....	16.2	2.24	1.7	7.3	2.0
Antimony.....	18.1	3.0	2.2	6.71	3.026
Iodine.....	25.7	2.0	13.0	4.95	4.73
Cæsium.....	70.6	0.95	61.0	1.89	4.216
Tantalum.....	10.93	4.75	0.54	16.6	3.156
Iridium.....	8.62	4.9	0.17	22.4	2.07
Platinum.....	9.1	4.36	0.21	21.3	1.926
Gold.....	10.2	3.4	0.47	19.24	2.218
Mercury.....	14.8	1.8	3.71	13.56	3.134
Thallium.....	17.2	1.84	2.6	11.83	2.634
Lead.....	18.2	1.84	2.2	11.4	2.429
Bismuth.....	21.2	1.63	2.8	9.8	2.32

by a thick line; corresponding elements in the different groups have been joined by dotted lines. The important correspondence between atomic volume and atomic number was brought out in 1870 by Lothar Meyer, and more recently relationships between κ and ν respectively with the atomic number have been demonstrated. The particular combination of these variables plotted in fig. 3 is of interest,

since the expression represents an energy ratio, and considerations of energy have always proved a powerful method of attack in physical problems.

Fig. 3.



The form of the curve is seen to be periodic, following closely the Mendeleef classification. It will be noticed, in contrast with the atomic volume curves of Meyer, that the halogen elements form the peaks. This seems in agreement with the pronounced chemical activity of the halogen family. The alkali metals lie on a well-defined line, the elements above which are all non-metals and the elements below which, with one exception, all metals. The exception is silicon (Group III.), which lies on the line through Pb, Sn, and Ge. It will be noticed, too, that carbon does not lie on this line, as it should according to its place in the Periodic Table, but has a much higher position. In this connexion it would be interesting to know the position boron occupies on the curve.

It has not been found possible to insert values for the inert elements, but they will in all probability be very small, on account of the smallness of their vibration frequency, and also of their compressibility at very low temperatures.

In conclusion, I wish to thank my wife for the valuable assistance she gave me during the preparation of the paper.

University of Leeds,
Aug. 10, 1923.

VIII. *A Note on Mr. Ablett's Paper on the Angle of Contact between Paraffin Wax and Water.* By ALLAN FERGUSON, M.A., D.Sc.*

IN the August number of the Philosophical Magazine, Mr. R. Ablett describes a series of ingenious and important experiments which gives the contact angle between paraffin wax and water. He finds that, for various speeds of rise or fall of the water-air surface, the contact angle (θ) corresponding to a stationary meniscus is connected with the angles (θ_1) and (θ_2) corresponding respectively to a rising and to a falling meniscus by the relation $2\theta = \theta_1 + \theta_2$. For speeds of rise or fall greater than about 0.5 mm./sec., θ_1 and θ_2 remain constant, but the same law holds.

This result, which has been tested for contact angles in the neighbourhood of 90° only, will undoubtedly have important bearings on the application of surface-tension theories to industrial problems, and it is much to be desired that Mr. Ablett should extend his measurements to include *small* contact angles.

With a not unnatural enthusiasm, but without any experimental justification, he extrapolates his law down to small contact angles, and endeavours to explain certain well-known phenomena in terms of this law.

Thus, in discussing certain experiments which I described to the Faraday Society some time ago, he says:—"Allan Ferguson, in 'Studies in Capillarity—II.' (Faraday Soc. Trans. 1921), dealing with a method of adjusting the air-pressure to force the meniscus down to the level of the free liquid surface, says:—"The presence or absence of a constant error was tested by taking the mean of the readings (1) when the meniscus just disappeared within the tube, (2) when it just protruded from the tube. The mean of these pressures agreed satisfactorily with the "crucial" pressure."

"The results given in the present paper explain this. Taking for granted that $\theta_2 = 0$ for water, θ_1 finite but small, then as before, $T \cos \theta$ should agree with $\frac{1}{2}(T \cos \theta_1 + T \cos \theta_2)$."

In the first place it should be noted that Mr. Ablett misapprehends the method. The air-pressure is adjusted so as to force the meniscus down to the *lower end* of a vertical capillary plunged into the liquid, and to hold it there in a

* Communicated by the Author.

stationary state. This process avoids the necessity for calibrating the tube, and incidentally minimises errors due to adsorption at the walls of the capillary; simple as the modification may be, it is a very different matter from forcing the meniscus "down to the level of the free liquid surface." This, however, by the way.

Even if we admit the legitimacy of Mr. Ablett's extrapolation, I see no reason for assuming, as he does, that $T \cos \theta$ must be equal to the mean of $T \cos \theta_1$ and $T \cos \theta_2$, subject to the condition that θ_2 is zero and θ_1 small. Under these circumstances Mr. Ablett's equation $2\theta = \theta_1 + \theta_2$ reduces to $\theta_1 = 2\theta$; the equation

$$2 \cos \theta = \cos \theta_1 + \cos \theta_2$$

reduces under similar circumstances, unless my algebra is very far astray, to $\theta_1 = \theta\sqrt{2}$ —not at all in accordance with his premisses.

Similar remarks apply to his discussion of the experiments of Hartley and Bosanquet. These experimenters do not state the formula which they employ for evaluating the contact angle from measurements of a large sessile drop. Assuming that they treat the radius of the drop as very large—at best a risky matter—and use a formula of the type

$$1 + \cos \theta = \frac{\rho g h^2}{2T} = Kl^2, \text{ say,}$$

where h is the total depth of the drop, it seems fairly obvious that Mr. Ablett's assumption [that under the circumstances of their experiment $\cos \theta = \cos \left(\frac{\theta_1 + \theta_2}{2} \right)$] leads to the result

that $h_1 + h_2/2h$ is *not* equal to unity. But as Mr. Ablett himself points out, $h_1 + h_2/2h$, as experimentally determined, is sensibly equal to unity. It would therefore seem that, as far as these experiments go, they point to a conclusion diametrically opposite to the one which he draws.

But this criticism is also incidental. The single and sufficient reason for rejecting Mr. Ablett's explanation is that it is not at all *ad rem*—and this on two counts. Mr. Ablett's experiments are essentially dynamical; the experiments which he discusses are statical in character. The symmetry of his own curves shows clearly that as the velocity decreases the angles θ_1 and θ_2 change *pari passu*, each approaching, from opposite sides, the stationary value θ , which is always symmetrically distant from corresponding

values of θ_1 and θ_2 . It would seem, therefore, that the correct interpretation of his results should be that a stationary meniscus should always occupy the same position in a tube whether it reach that position by rising or by falling. This is *not* in accordance with the experience of other workers—compare the quotation from Harkins and Brown's paper which is given by Mr. Ablett—and since his curves are extrapolated between zero and a velocity of 0.13 mm. per second, it seems desirable to carry out experiments at velocities between these limits in order to examine whether any tendency to asymmetry exists within this region.

Again, granting all his premisses, his explanation of the phenomena recorded in my paper only applies if one reading be taken with a falling, one with a rising meniscus, the crucial pressure being read with a stationary meniscus. Obviously these readings, made as they were merely to test the sensitiveness of the setting, were not taken in this highly artificial order. There is no suggestion of any such order in my text, neither were the readings taken with a moving meniscus. The obvious order of experiment, and the order in which the readings were taken, was:—the tube being immersed vertically in the liquid under test, the liquid rose in the tube. The liquid in the tube was then forced down until the meniscus was just short of appearing at the lower end (pressure head $h - \delta h$), then until it was just flush with the end (h), then until the end of the meniscus just protruded ($h + \delta h$). *For each reading, the meniscus was held stationary.* The statement in my text simply asserts that $\delta h = \delta h'$ —or, to quote an analogous geometrical problem, in fixing accurately the position of a point on a curve it is possible to draw a chord so close to the tangent at the point that the chord intercepts equal arcs on each side of the point. It is a mere test of accuracy of setting and, with readings taken in this order, no question of contact angles arises.

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a centre C, and O the c.g. of the body describes another horizontal circle about a centre B, in the vertical line CB.

Produce CB up to A, where AB= λ is the height of the conical pendulum AO, revolving in the same period as a circuit of O.

The reaction S of the table will act through P parallel to OA, and the body being an M lb weight, the vertical component of S is M lb, and the moment of S about O is M.OB (ft.-lb), if S crosses the horizontal OB in D, a distance OD feet.

The axis Oz of the body crosses BC in a fixed point E, and EP is the instantaneous axis of rotation in the steady motion, with $OE = \frac{b}{\sin \theta}$; and then if P, R denote the components of angular velocity of the body about Ox, Oz,

$$\frac{R}{P} = \frac{EN}{NP} = \frac{z - \frac{b}{\sin \theta}}{x}, \text{ with } P = \mu \sin \theta, \quad (1)$$

if μ denotes the precessional velocity, so that

$$\frac{R}{\mu} = \frac{z \sin \theta - b}{x}; \quad \text{also} \quad \lambda = \frac{g}{\mu^2}. \quad (2)$$

The components of angular momentum (A.M.) are then AP= $A\mu \sin \theta$ about Ox, and $h_3 = CR + K$ about Oz, the constant term K being added to allow for the A.M. of a flywheel K, on a smooth axle fixed in the axis Oz or parallel to it, forming part of the body.

Representing these components of A.M. vectorially to scale by kh and ho , so that Ok is the vector of resultant A.M., the velocity of k must be equated to the impressed couple, or with Og the vector component of A.M. about the vertical OY,

$$\mu . gk = gM . OD = \mu^2 \lambda . OD, \quad (3)$$

$$\mu h_3 \sin \theta - \mu^2 A \sin \theta \cos \theta = M \mu^2 \lambda . OD; \quad (4)$$

and denoting OY by p and YP by q , then

$$pb = \lambda . YF, \quad pb + q\lambda = \lambda . PF = \lambda . OD, \quad (5)$$

$$\frac{h_3}{M\mu} = \frac{A}{M} \cos \theta + \frac{\lambda . OD}{\sin \theta} = \frac{A}{M} \cos \theta + \frac{pb + q\lambda}{\sin \theta}. \quad (6)$$

Written as a quadratic in μ , with $b = z \sin \theta - \frac{Rx}{\mu}$,

$$\mu^2 \left(\frac{A}{M} \cos \theta + pz \right) - \mu \left(R \frac{px}{\sin \theta} + \frac{h_3}{M} \right) + \frac{gq}{\sin \theta} = 0, \quad (7)$$

$$\begin{aligned} & \left[2\mu \left(\frac{A}{M} \cos \theta + pz \right) - R \frac{px}{\sin \theta} - \frac{h_3}{M} \right]^2 \\ &= \left(\frac{Rpx}{\sin \theta} + \frac{h_3}{M} \right)^2 - 4g \left(\frac{A}{M} \cos \theta + pz \right) \frac{q}{\sin \theta}, \quad (8) \end{aligned}$$

and the right-hand side must be positive, or vanishes in the critical state of Steady Motion, when the wobble begins.

Thus spun upright, with $p=z, x=0$, but on a rounded end like an egg-shaped body, $\frac{x}{\sin \theta} = \rho$, the radius of curvature at the end, $\frac{q}{\sin \theta} = z - \rho$; and with $K=0, h_3=CR$ in a solid body, the wobble begins when

$$R^2 \left(z\rho + \frac{C}{M} \right)^2 = 4g \left(\frac{A}{M} + z^2 \right) (z - \rho) \quad (9)$$

and the critical energy is then

$$\frac{CR^2}{2g} = \frac{2C \left(\frac{A}{M} + z^2 \right) (z - \rho)}{\left(\frac{C}{M} + z\rho \right)^2}, \quad (10)$$

as in Routh's 'Advanced Rigid Dynamics,' p. 202.

2. In a general state of Unsteady Motion of the body, rolling about anyhow on the table, the equations are referred to moving axes in the figure 1, Ox, Oy, Oz , with U, V, W the components of linear velocity of O ; P, Q, R of angular velocity (A.V.); h_1, h_2, h_3 of A.M.; and $\theta_1, \theta_2, \theta_3$ the components of A.V. of the frame of reference $Oxyz$, not fixed in the body except that Oz is in coincidence with the axis of the body.

Then with x, y, z the coordinates of P the point of contact with the table; X, Y, Z the components (in absolute measure) of the reaction at P of the table on the body; α, β, γ the direction cosines of the downward vertical OY , normal to the table, the geometrical relations, expressing that the point of contact P is at rest for the moment on the table, are:

$$U - Ry + Qz = 0, \quad V - Pz + Rx = 0, \quad W - Qx + Py = 0. \quad (1)$$

The general dynamical equations are :

$$\frac{dU}{dt} - V\theta_3 + W\theta_2 = \frac{X}{M} + g \sin \theta, \quad (2)$$

$$\frac{dV}{dt} - W\theta_1 + U\theta_3 = \frac{Y}{M}, \quad (3)$$

$$\frac{dW}{dt} - U\theta_2 + V\theta_1 = \frac{Z}{M} + g \cos \theta, \quad (4)$$

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 = yZ - zY, \quad (5)$$

$$\frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 = zX - xZ, \quad (6)$$

$$\frac{dh_3}{dt} - h_1\theta_2 + h_2\theta_1 = xY - yX, \quad (7)$$

and the elimination of X, Y, Z, the reaction components, will lead to the differential equations of motion.

3. In our special case where the surface of the body is of revolution about Oz, and the body is kinetically symmetrical about Oz as a principal axis, we take Oy horizontal and the plane Ozx through P the point of contact with the table; so that $y=0$, $\beta=0$; and eliminating at the outset the components of reaction, X, Y, Z,

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 + Mz \left(\frac{dV}{dt} - W\theta_1 + U\theta_3 \right) = 0, \quad (1)$$

$$\frac{dh_3}{dt} - h_1\theta_2 + h_2\theta_1 - Mx \left(\frac{dV}{dt} - W\theta_1 + U\theta_3 \right) = 0, \quad (2)$$

$$\begin{aligned} \frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 - Mz \left(\frac{dU}{dt} - V\theta_3 + W\theta_2 \right) \\ + Mx \left(\frac{dW}{dt} - U\theta_2 + V\theta_1 \right) + gM(z\alpha - x\gamma) = 0. \end{aligned} \quad (3)$$

Denoting the Precession of the axes about the vertical by μ , variable in Unsteady Motion where the angle θ is variable between Oz and the downward vertical,

$$\left. \begin{aligned} \alpha &= \sin \theta, & \beta &= 0, & \gamma &= \cos \theta; \\ h_1 &= AP, & h_2 &= AQ, & h_3 &= CR + K. \end{aligned} \right\} (4)$$

The constant K is added to allow for the influence of a flywheel on a smooth axle fixed in the body in the axis Oz,

or parallel to it; and K remains constant during the motion although the axle changes in direction.

A large flywheel concealed in such a body is called a Gyrostat; it can be handled to feel the gyroscopic effect; or made useful on a large scale for controlling the rolling motion of a ship, or as in the Gyrocompass for steering it.

The axis Oz being fixed in the body, and the precession being reckoned clockwise on the table,

$$\theta_1 = P = \mu \sin \theta, \quad \theta_2 = Q = -\frac{d\theta}{dt}, \quad \theta_3 = \mu \cos \theta; \quad \dots \quad (5)$$

but θ_3 and R are different, because the frame of reference, $Oxyz$, rotates about Oz relatively to the body and independently.

With $y = 0$, the geometrical relations reduce to

$$U = -Qz, \quad V = Pz - Rx, \quad W = Qx. \quad \dots \quad (6)$$

Thus, with

$$P = \mu \sin \theta, \quad Q = -\frac{d\theta}{dt}, \quad \text{but } R \text{ not } \mu \cos \theta; \quad \dots \quad (7)$$

$$\theta_1 = P, \quad \theta_2 = Q, \quad \theta_3 = \mu \cos \theta; \quad \dots \quad (8)$$

$$h_1 = AP, \quad h_2 = AQ, \quad h_3 = CR + K; \quad \dots \quad (9)$$

and ρ denoting the radius of curvature PR of the meridian curve at P ,

$$\frac{dx}{dt} = -Q\rho \cos \theta, \quad \frac{dy}{dt} = 0, \quad \frac{dz}{dt} = Q\rho \sin \theta, \quad \dots \quad (10)$$

$$\begin{aligned} \frac{dV}{dt} - W\theta_1 + U\theta_3 &= \frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x - 2Q\mu z \cos \theta \\ &\quad - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta, \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{dU}{dt} - V\theta_3 + W\theta_2 &= -\frac{dQ}{dt} z + Q^2(x - \rho \sin \theta) \\ &\quad - \mu^2(z \sin \theta - x \cos \theta) \cos \theta, \end{aligned} \quad \dots \quad (12)$$

$$\begin{aligned} \frac{dW}{dt} - U\theta_2 + V\theta_1 &= \frac{dQ}{dt} x + Q^2(z - \rho \cos \theta) \\ &\quad + \mu^2(z \sin \theta - x \cos \theta) \sin \theta, \end{aligned} \quad \dots \quad (13)$$

$$\frac{dh_1}{dt} - h_2\theta_3 + h_3\theta_2 = A \frac{d\mu}{dt} \sin \theta - 2AQ\mu \cos \theta + Qh_3, \quad \dots \quad (14)$$

$$\frac{dh_2}{dt} - h_3\theta_1 + h_1\theta_3 = A \frac{dQ}{dt} + A\mu^2 \sin \theta \cos \theta - h_3\mu \sin \theta, \quad \dots \quad (15)$$

$$\frac{dh_3}{dt} - h_1\theta_2 + h_2\theta_1 = C \frac{dR}{dt}. \quad \dots \quad (16)$$

Introducing these values into (1) and (2),

$$\begin{aligned} A \frac{d\mu}{dt} \sin \theta - 2AQ\mu \cos \theta + Qh_3 + Mz \left[\frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x \right. \\ \left. - 2Q\mu z \cos \theta - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta \right] = 0, \\ C \frac{dR}{dt} - Mx \left[\frac{d\mu}{dt} z \sin \theta - \frac{dR}{dt} x - 2Q\mu z \cos \theta \right. \\ \left. - Q\mu(x - \rho \sin \theta) \sin \theta + QR\rho \cos \theta \right] = 0, \\ \left(\frac{A}{M} + z^2 \right) \frac{d\mu}{dt} \sin \theta - xz \frac{dR}{dt} - Q\mu \left[2 \left(\frac{A}{M} + z^2 \right) \cos \theta \right. \\ \left. + (x - \rho \sin \theta) z \sin \theta \right] + QR\rho z \cos \theta + Q \frac{h_3}{M} = 0, \quad (17) \end{aligned}$$

$$\begin{aligned} \left(\frac{C}{M} + x^2 \right) \frac{dR}{dt} - xz \frac{d\mu}{dt} \sin \theta + Q\mu [(x - \rho \sin \theta)x \sin \theta \\ + 2xz \cos \theta] - QR\rho x \cos \theta = 0, \quad (18) \end{aligned}$$

two simultaneous differential equations (D.E.) of the first order for the determination of μ and R , or $CR + K = h_3$; thence two separate D.E.'s of the second order.

They are of intractable nature in general, although some cases are mentioned in the Report on Gyroscopic Theory, 1914 (R.G.T.), where the character is hyperelliptic or hypergeometrical, and so may be considered tractable to a certain extent.

4. The reduction of (3) § 3 leads to

$$\begin{aligned} \frac{dQ}{dt} \left(\frac{A}{M} + x^2 + z^2 \right) + Q^2 q\rho + \mu^2 \frac{A}{M} \sin \theta \cos \theta + \mu^2 p z \sin \theta \\ - \mu R p x - \mu \frac{h_3}{M} \sin \theta + gq = 0, \quad (1) \end{aligned}$$

with

$$z \cos \theta + x \sin \theta = p, \quad z \sin \theta - x \cos \theta = q = -\frac{dp}{d\theta},$$

so that

$$\begin{aligned} p - \frac{dq}{d\theta} = p + \frac{d^2 p}{d\theta^2} = \rho, \quad \frac{dq}{d\theta} = p - \rho, \\ \frac{dx}{d\theta} = +\rho \cos \theta, \quad \frac{dz}{d\theta} = -\rho \sin \theta. \end{aligned}$$

This equation (1), combined with (17), (18) § 3, will lead

to an equation—the Equation of Energy; and further integration is intractable.

But differentiating (1) with respect to θ , with $d\theta = -Qdt$, an equation is obtained in the general state of Unsteady Motion of the form

$$a_1 + b_1 \frac{d\mu}{\mu d\theta} \sin \theta + c_1 \frac{dR}{\mu d\theta} = 0, \quad (2)$$

$$a_1 = -\frac{d^2 Q}{\mu^2 Q d\theta^2} \left(\frac{A}{M} + x^2 + z^2 \right) + \frac{1}{\mu^2} \frac{d}{d\theta} (Q^2 q \rho) + \frac{A}{M} \cos 2\theta \\ + pz \cos \theta - qz \sin \theta - p\rho \sin^2 \theta \\ + \frac{R}{\mu} (qx - p\rho \cos \theta) - \frac{h_3}{M\mu} \cos \theta + \lambda(p - \rho), \quad . . . (3)$$

$$b_1 = 2 \frac{A}{M} \cos \theta + 2pz - \frac{R}{\mu} \frac{px}{\sin \theta} - \frac{h_3}{M\mu}, \quad (4)$$

$$c_1 = -p\rho - \frac{C}{M} \sin \theta. \quad (5)$$

Re-writing (17), (18) § 3 in the form

$$a_2 + b_2 \frac{d\mu}{\mu d\theta} \sin \theta + c_2 \frac{dR}{d\theta} = 0, \quad (6)$$

$$a_3 + b_3 \frac{d\mu}{\mu d\theta} \sin \theta + c_3 \frac{dR}{d\theta} = 0, \quad (7)$$

$$a_2 = 2 \left(\frac{A}{M} + z^2 \right) \cos \theta + (x - \rho \sin \theta) z \sin \theta - \frac{R}{\mu} z \rho \cos \theta - \frac{h_3}{M\mu}, \quad . . . (8)$$

$$b_2 = \frac{A}{M} + z^2, \quad c_2 = -xz; \quad (9)$$

$$a_3 = -(x - \rho \sin \theta) x \sin \theta - 2xz \cos \theta + \frac{R}{\mu} x \rho \cos \theta, \quad . . . (10)$$

$$b_3 = -xz, \quad c_3 = \frac{C}{M} + x^2; \quad (11)$$

the determinant $(a_1 \ b_2 \ c_3)$, result of the elimination of $\frac{d\mu}{\mu d\theta} \sin \theta$ and $\frac{dR}{d\theta}$, as in Routh's 'Advanced Rigid Dynamics,' p. 192, will lead to the equation for $\frac{d^2 Q}{Q d\theta^2}$ requiring an integration of the previous equations.

Here is an exact equation of the general Unsteady Motion in an Antepenultimate State.

But these considerations, a contribution more to Scientific Method than advance of Scientific Thought, would lead us far beyond our scope, limited to the investigation of the Precession in Steady Motion, and a small Nutation superposed.

$$\begin{aligned}
 D \frac{dR}{\mu d\theta} &= \frac{A}{M}(x - \rho \sin \theta)x \sin \theta - \frac{R}{\mu} \frac{A}{M} x \rho \cos \theta + \frac{h_3}{M\mu} xz \\
 &= \frac{A}{M} \{p(x - \rho \sin \theta) + b\rho \cos \theta\} + xz \frac{pb + q\lambda}{\sin \theta} \\
 &= + \frac{A}{M} x \cdot RQ + xz \frac{pb + q\lambda}{\sin \theta} \dots \dots \dots (7)
 \end{aligned}$$

(λ.O.D.)

This is with R and h_3 exterminated; but retaining them and exterminating b , when we wish to obtain Routh's result for a disk.

$$\text{Here} \quad p(x - \rho \sin \theta) + b\rho \cos \theta = x \cdot BQ, \quad \dots \dots (8)$$

if TR produced through R the centre of curvature cuts BC in Q in fig. 1; and then

$$\begin{aligned}
 a_1 &= \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) - \frac{A}{M} \sin^2 \theta - p^2 - bq + pz \cos \theta \\
 &\quad - q\lambda \cot \theta + \lambda(p - c) - (pb + q\lambda) \cot \theta + p \cdot BQ, \quad (9)
 \end{aligned}$$

$$a_2 = \left(\frac{A}{M} + z^2 \right) \cos \theta - \frac{pb + q\lambda}{\sin \theta} + z \cdot BQ, \quad \dots \dots \dots (10)$$

$$a_3 = -xz \cos \theta - x \cdot BQ, \quad \dots \dots \dots (11)$$

$$\begin{aligned}
 &a_1 - a_2 \cos \theta + a_3 \sin \theta \\
 &= \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) - \frac{A}{M} - p^2 - bq - q\lambda \cot \theta \\
 &\quad + \lambda(p - \rho) + p \cdot BQ. \quad (12)
 \end{aligned}$$

Then the determinant of § 4

$$\begin{aligned}
 &a_1(b_2c_3 - b_3c_2) + a_2(b_3c_1 - b_1c_3) + a_3(b_1c_2 - b_2c_1) \\
 &= D(c_1 - a_2 \cos \theta + a_3 \sin \theta) \\
 &\quad + \frac{q\lambda}{\sin \theta} \left[\left(\frac{C}{M} + x^2 \right) a_2 + xz a_3 \right] = 0, \quad (13)
 \end{aligned}$$

and

$$\begin{aligned}
 &\left(\frac{C}{M} + x^2 \right) a_2 + xz a_3 \\
 &= \left(\frac{C}{M} + x^2 \right) \left[\left(\frac{A}{M} + x^2 \right) \cos \theta + z \cdot BQ - \frac{pb + q\lambda}{\sin \theta} \right] \\
 &\quad - x^2 z^2 \cos \theta - x^2 z \cdot BQ \\
 &= D \cos \theta + \frac{C}{M} z \cdot BQ - \left(\frac{C}{M} + x^2 \right) \frac{pb + q\lambda}{\sin \theta} \dots \dots \dots (14)
 \end{aligned}$$

The minor determinants of $(a_1 b_2 c_3)$ in § 4 are :

$$b_2 c_3 - b_3 c_2 = D,$$

$$b_3 c_1 - b_1 c_3 = -D \cos \theta + \left(\frac{C}{M} + z^2 \right) \frac{q\lambda}{\sin \theta},$$

$$b_1 c_2 - b_2 c_1 = D \sin \theta + xz \frac{q\lambda}{\sin \theta}; \quad . \quad . \quad (15)$$

and so the complete determinant is

$$D(a_1 - a_2 \cos \theta + a_3 \sin \theta) + \left[\left(\frac{C}{M} + x^2 \right) a_2 + xz a_3 \right] \frac{q\lambda}{\sin \theta}, \quad (16)$$

leading to the simple equation for $\frac{m^2}{\mu^2}$ or $\frac{\lambda}{L}$,

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D = D \left(\frac{A}{M} + p^2 + bq - q\lambda \cot \theta \right) - D\lambda(p - \rho) \\ - \frac{C}{M} z \cdot BQ \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \frac{pb + q\lambda}{\sin \theta} \cdot \frac{q\lambda}{\sin \theta}. \quad (A) \end{aligned}$$

involving geometrical lengths only, as g has been exterminated by the introduction of an E.S.P. (equivalent in

simple pendulum) length $\lambda = \frac{g}{\mu^2}$, $L = \frac{g}{m^2}$ fundamental in our subject.

Then $\frac{A}{M}$, $\frac{C}{M}$ can be measured experimentally by swinging

the body as a pendulum about the axis PN, PM, and noting the length of the E.S.P. l_1 , l_3 , making

$$\frac{A}{M} + z^2 = l_1 z, \quad \frac{C}{M} + x^2 = l_3 x, \quad D = xz(l_1 l_3 - xz); \quad \text{also}$$

$\frac{A}{M} + x^2 + z^2 = l \cdot OP$, by swinging the body about an axis through P parallel to Oy.

The result is independent of the local g , or density of the body, so that the determinant is a relation between algebraical symbols of length only. No time measurement required and no unit of weight or weighing, as the density does not intervene.

To make a simple pendulum to measure l the length of the E.S.P. with accuracy, take a sphere W with a diametral hole, and pass a fine smooth thread through it,

Expressed in (A) by powers of $\frac{q\lambda}{\sin \theta}$, and h_3 replaced by $z \sin \theta - \frac{R}{\mu} x$,

$$\begin{aligned} & \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D \\ = & D \left(\frac{A}{M} + p^2 + q^2 \right) - D\lambda(p - \rho) - \left[D \cos \theta + \frac{C}{M} \cdot \text{ON} \cdot \text{BQ} \right. \\ & \left. - \left(\frac{C}{M} + x^2 \right) \rho \left(z - \frac{R}{\mu} \frac{x}{\sin \theta} \right) \right] \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \left(\frac{q\lambda}{\sin \theta} \right)^2. \end{aligned} \quad \dots (B)$$

6. The body can roll round in a circle with the axis horizontal when it has bias, so that z is not zero, and then

$$\theta = \frac{1}{2}\pi, \quad p = x, \quad q = z, \quad \frac{R}{\mu} = \frac{z - b}{x}, \quad \text{BQ} = x - \rho,$$

as BQ is horizontal; and then in (A),

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D = & D \left(\frac{A}{M} + x^2 + bz \right) - D\lambda(x - \rho) \\ & - \frac{C}{M} z(x - \rho)z\lambda + \left(\frac{C}{M} + x^2 \right) (bx + z\lambda)z\lambda. \end{aligned} \quad (1)$$

With no bias, $z=0$, $\mu=0$, and the path over the table is straight, with a slight sinuosity, where in (A), (B),

$$m^2 \left(\frac{A}{M} + x^2 \right) = \frac{h_3}{A} \left(Rx + \frac{h_3}{M} \right) - g(x - \rho). \quad \dots (2)$$

As a solid body, with $K=0$, $h_3=CR$,

$$\frac{m^2}{R^2} \left(\frac{A}{M} + x^2 \right) = \frac{C}{A} \left(\frac{C}{M} + x^2 \right) - \frac{g}{R^2} (x - \rho), \quad \dots (3)$$

and there are m sinuosities in R revolutions.

As a Kelvin gyrostat, a flywheel concealed in a cover with a sharp edge, placed on the table the body can hold itself upright with the axle horizontal and $\mu=0$, $R=0$; stationary apparently except for a slight imperceptible oscillation,

swaying $\frac{m}{\pi}$ times per second, where

$$m^2 = \frac{\frac{K^2}{MA} - g(x - \rho)}{\frac{A}{M} + x^2}, \quad . \quad . \quad . \quad (4)$$

if the flywheel is spun with A.M. K ; and m^2 must be positive for this upright position to be stable.

So too for a solid body like a biscuit or curtain-ring, spun about a vertical diameter with A.V. μ ,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} + x^2 - \lambda(x - \rho) \quad . \quad . \quad . \quad (5)$$

and the energy $\frac{A\mu^2}{2g}$ must then exceed $\frac{\frac{1}{2}M(x - \rho)}{1 + \frac{Mx^2}{A}}$ for the stability of the motion.

Spinning upright on one end, with $\theta = 0$, $x = 0$, but $\frac{g\lambda}{\sin \theta} = PG = \rho$, $\frac{g}{\sin \theta} = OG = z - \rho$, $\rho = z$, $D = \frac{C}{M} \left(\frac{A}{M} + z^2 \right)$, $BQ = \rho \left(1 - \rho \frac{\sin \theta}{x} \right) + \rho \left(z \frac{\sin \theta}{x} - \frac{R}{\mu} \right) = z - \frac{R}{M} \rho = \frac{b}{\sin \theta}$, with $b = 0$; and dividing out $\frac{C}{M}$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + z^2 \right)^2 = \left[\frac{A}{M} + z^2 - \lambda(z - \rho) \right]^2 \quad . \quad . \quad . \quad (6)$$

With the Steady Motion condition of § 1, and $h_3 = CR$,

$$\frac{g\lambda}{\sin \theta} = \lambda(z - \rho) = \frac{h_3}{M\mu} - \frac{A}{M} - \frac{pb}{\sin \theta} = \left(\frac{C}{M} + z\rho \right) \frac{R}{\mu} - \frac{A}{M} - z^2, \quad . \quad . \quad . \quad (7)$$

$$\frac{m}{\mu} = \frac{\frac{A}{M} + z^2 - \lambda(z - \rho)}{\frac{A}{M} + z^2} = \frac{2 \left(\frac{A}{M} + z^2 \right) - \left(\frac{C}{M} + z\rho \right) \frac{R}{\mu}}{\frac{A}{M} + z^2}, \quad . \quad (8)$$

$$\frac{m}{R} = \frac{2 \frac{\mu}{R} \left(\frac{A}{M} + z^2 \right) - \frac{C}{M} - z\rho}{\frac{A}{M} + z^2} = \frac{\frac{C}{M} + z\rho}{\frac{A}{M} + z^2} \cdot \frac{\frac{A}{M} - \lambda(z - \rho)}{\frac{A}{M} + \lambda(z - \rho)}; \quad (9)$$

and the axis oscillates, swaying slightly to and fro, m times in R revolutions of the body.

In the special case where the centre O is at rest, $b=0$, as in Routh, ex. 2, p. 197, for the disk, and OP is the axis of instantaneous rotation, $\frac{R}{\mu} = \frac{z}{x} \sin \theta$, $x \cdot BQ = p(x - \rho \sin \theta)$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 + z^2 \right) D = D \left(\frac{A}{M} + p^2 \right) - D\lambda(p - \rho) - Dq\lambda \cot \theta \\ - \frac{C}{M} z p \left(1 - \frac{\rho}{x} \sin \theta \right) \frac{q\lambda}{\sin \theta} + \left(\frac{C}{M} + x^2 \right) \left(\frac{q\lambda}{\sin \theta} \right)^2, \quad (10)$$

and in the Steady Motion condition,

$$\frac{q\lambda}{\sin \theta} = \frac{h_3}{M\mu} - \frac{A}{M} \cos \theta. \quad . \quad . \quad . \quad (11)$$

Then for the disk of Routh, $z=0$, $p=x \sin \theta$, $q=-x \cos \theta$,

$$R=0, h_3=0, \frac{A}{M} = \frac{\lambda x}{\sin \theta}, \lambda x = \frac{A}{M} \sin \theta,$$

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} + x^2 \sin^2 \theta + \lambda x \frac{\cos^2 \theta}{\sin \theta} \\ - \lambda x \sin \theta + \frac{\frac{C}{M} + x^2}{D} \lambda^2 x^2 \cot \theta \\ = \frac{A}{M} + x^2 \sin^2 \theta + \frac{A}{M} \cos^2 \theta - \frac{A}{M} \sin^2 \theta + \frac{A}{M} \cos^2 \theta \\ = 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta, \quad . \quad . \quad . \quad (12)$$

$$L = \frac{g}{m^2} = \frac{A}{Mx} \cdot \frac{\left(\frac{A}{M} + x^2 \right) \sin \theta}{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}, \quad . \quad . \quad . \quad (13)$$

in agreement with Routh.

7. Tested for the previous case in Phil. Mag. March 1923 of the spinning top on a sharp point, $\rho=0$, in which K can be lumped up with CR in h_3 ,

$$x=0, b=q=z \sin \theta, p=z \cos \theta, BQ=0, D = \frac{C}{M} \left(\frac{A}{M} + z^2 \right);$$

and dividing out $\frac{C}{M}$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + z^2 \right)^2 = \left(\frac{A}{M} + z^2 \right)^2 - 2 \left(\frac{A}{M} + z^2 \right) z \lambda \cos \theta + z^2 \lambda^2. \quad (1)$$

Then, as in Phil. Mag. July 1922, p. 387, with O at the point of the top in a small smooth cup, and $OP=l$, $l^2 = \frac{A}{M} + z^2$, $OA=\lambda$, drawn vertically upward in the figure there;

$$\frac{m^2}{\mu^2} = \frac{\lambda}{L} = 1 - 2 \frac{\lambda}{l} \cos \theta + \frac{\lambda^2}{l^2} = \frac{AP^2}{OP^2}, \quad \dots \quad (2)$$

and the nutations of the axle are to the circuits round the vertical in the ratio of AP to OP.

To cut off on OA the length $OL=L$, describe the circle AOE through O and A touching OP at O, and crossing PA in E; then EL parallel to OP will cut off OL. For

$$\frac{OP^2}{AP^2} = \frac{AP \cdot PE}{AP^2} = \frac{PE}{AP} = \frac{OL}{OA}, \quad \dots \quad (3)$$

as required.

In the Steady Motion of the top round the vertical,

$$\begin{aligned} \frac{CR\mu}{M} &= \mu^2 \frac{A}{M} \cos \theta + g \cdot OG \\ &= \mu^2 \frac{A}{M} \cos \theta + n^2 \cdot OG \cdot OP = \frac{A}{M} (\mu^2 \cos \theta + n^2), \end{aligned} \quad (4)$$

$$\frac{CR}{An} = \frac{\mu}{n} \cos \theta + \frac{n}{\mu}; \quad \dots \quad (5)$$

and taking $n^2 = p^2 \cos \theta$, $\frac{\mu^2}{n^2} = \frac{OP}{OA}$, $\frac{\mu^2}{p^2} = \frac{OH}{OA}$,

$$\frac{\mu}{p} + \frac{p}{\mu} = \sqrt{\frac{OH}{OA}} + \sqrt{\frac{OA}{OH}} = \cot \alpha + \tan \alpha = \sin 2\alpha, \quad (6)$$

$$\text{with } \sin 2\alpha = \frac{2Ap}{CR}, \quad \frac{OH}{OA} = \tan \alpha.$$

Then if QQ' is drawn vertical in fig. 2 to cross the circle on OH in Q, Q', at a distance from AH in the ratio to OH of $2Ap$ to CR , and HQ is produced to meet the horizontal through O in R, the circle through R and H touching OR

at R will cut off a length OA, and make the angles ORA and OHR equal.

The same method can be extended to the rolling body of § 1; and there in fig. 1, with

$$\frac{A}{M} = OE \cdot OS, \quad g = n^2 \cdot OS = p^2 \cdot OH, \quad \dots \quad (7)$$

the Steady Motion condition can be written

$$\frac{\mu}{p} + \frac{p}{\mu} = \frac{h_3}{Ap}, \quad \dots \quad (8)$$

with the same geometrical construction for $\lambda = AB$.

But there does not appear to be any similar geometrical interpretation of $L = \frac{g}{m^2}$ for the nutation.

8. For a sharp edge, as of a coin, canister, wine-glass, put $\rho = 0$; but this does not introduce much simplification in the general case.

If, however, $z = 0$ as well, we have the case of a disk rolling on a plane, discussed by Routh in his ex. 3, p. 197; and then

$$p = x \sin \theta, \quad q = -x \cos \theta, \quad D = \frac{A}{M} \left(\frac{C}{M} + x^2 \right), \quad \dots \quad (1)$$

and dividing out $\frac{C}{M} + x^2$ in (A) § 5,

$$\begin{aligned} & \frac{m^2}{\mu^2} \frac{A}{M} \left(\frac{A}{M} + x^2 \right) \\ &= \frac{A}{M} \left(\frac{A}{M} + x^2 \sin^2 \theta - bx \cos \theta + \lambda x \frac{\cos^2 \theta}{\sin \theta} - \lambda x \sin \theta \right) \\ & \quad - \frac{bx \sin \theta - \lambda x \cos \theta}{\sin \theta} \cdot \frac{\lambda x \cos \theta}{\sin \theta}, \quad \dots \quad (2) \end{aligned}$$

with

$$\lambda x \cot \theta = \frac{A}{M} \cos \theta - \left(\frac{C}{M} + x^2 \right) \frac{R}{\mu},$$

$$bx - \lambda x \cot \theta = -\frac{A}{M} \cos \theta + \frac{CR}{M\mu}, \quad \frac{b}{x} = -\frac{R}{\mu}, \quad \dots \quad (3)$$

and then

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = \frac{A}{M} (1 + 2 \cos^2 \theta) + x^2 \sin^2 \theta - \frac{R}{\mu} \cos \theta \left(3 \frac{C}{M} + x^2 \right) + \frac{C}{A} \left(\frac{C}{M} + x^2 \right) \frac{R^2}{\mu^2} - \frac{gx}{\mu^2} \sin \theta, \quad (4)$$

in agreement with Routh, when $C=2A$, in the thin disk.

But in Routh's result there is a redundancy of quantities ; so replacing

$$\frac{gx \sin \theta}{\mu^2} = \lambda x \sin \theta \text{ by } \frac{A}{M} \sin^2 \theta - \frac{R}{\mu} \left(\frac{C}{M} + x^2 \right) \frac{\sin^2 \theta}{\cos \theta}, \quad (5)$$

$$\begin{aligned} \frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) &= 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta \\ &\quad - \left[\frac{C}{M} (4 \cos \theta - \sec \theta) + x^2 (2 \cos \theta - \sec \theta) \right] \frac{R}{\mu} \\ &\quad + \frac{C}{A} \left(\frac{C}{M} + x^2 \right) \frac{R^2}{\mu^2} \quad . \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

Then, in Routh's example 2, p. 197, where $b=0$, $R=0$,

$$\frac{m^2}{\mu^2} \left(\frac{A}{M} + x^2 \right) = 3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta, \quad . \quad . \quad . \quad (7)$$

$$\begin{aligned} m^2 &= \frac{gMx}{A} \frac{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}{\left(\frac{A}{M} + x^2 \right) \sin \theta}, \\ L &= \frac{A}{Mx} \frac{\left(\frac{A}{M} + x^2 \right) \sin \theta}{3 \frac{A}{M} \cos^2 \theta + x^2 \sin^2 \theta}, \quad . \quad . \quad . \quad (8) \end{aligned}$$

in agreement, for $\frac{n}{\pi}$ beats per second.

X. *The Molecular Association of Liquids and Highly-Compressed Gases.*—Parts I. and II. By E. E. WALKER, D.Sc., D.I.C., A.C.G.I.*

PART I.—MOLECULAR ASSOCIATION AT THE CRITICAL POINT.

THE determination of the degree of molecular association of liquids presents considerable difficulties because the laws governing the properties of liquids are very imperfectly understood. It is on this account that most methods of determining the association factor of liquids depend directly or indirectly on the law of corresponding states, which is itself only a rough approximation. Unfortunately, errors much larger than those due to the inaccuracy of this law are generally introduced by neglecting the fact that the critical pressure and temperature to which an associated liquid at the temperature T should be referred are *not* the observed critical constants, but those which would have been observed if the substance had been raised from the temperature T to the critical point without any change in the degree of association taking place. Batschinski† recognized this fact, but his method of determining this hypothetical critical temperature does not appear to have been very satisfactory, and the modification of the Eötvös equation to which his theories led him gave unsatisfactory results.

In this series of papers the author proposes to study the effect of molecular size on the critical constants, and to use the knowledge thus obtained to calculate the association factor of liquids from a modified law of corresponding states.

According to van der Waals's equation the critical temperature is proportional to $\frac{a}{b}$. If we assume that the molecular attractive power " a " and the molecular volume " b " are doubled when one molecule combines with another of the same sort to form a double molecule, then the critical temperature should remain unaffected. This is contrary to all accepted belief, and there can be no doubt at all that the boiling-point and critical point are, in fact, raised by molecular association. Since the space occupied by the double molecule must be practically double that occupied by the single molecule, we are driven to the conclusion either that

* Communicated by the Author.

† A. Batschinski, *Zeit. Phys. Chem.* lxxv. p. 665 (1911), and lxxxii. pp. 86 and 90 (1913); for another method see xl. p. 629 (1902).

the molecular attractive power is increased by combination or that van der Waals's equation misrepresents the facts. The first alternative seems improbable, and, since van der Waals's equation is known to be inaccurate at the critical point, the second alternative has been accepted. On this account, and in order to explain a variety of phenomena, the following modified equation of state has been adopted :

$$\left(P + \frac{a}{V^{2/3}}\right)(V-b) = RT. \quad . \quad . \quad . \quad (1)$$

This equation was first suggested by P. de Heen in 1887, and has been examined by Dieterici and others*. It has the advantage of being very much more accurate than van der Waals's equation in the neighbourhood of the critical point, but it fails for gases under moderate pressures. According to this equation the value of the critical coefficient $\frac{RT_c}{P_c V_c}$ should be 3.75, and this was the mean value found by Young for a number of organic compounds, while van der Waals's equation requires that it should have a value of $2\frac{2}{3}$.

The author was led to adopt Dieterici's equation in the first place because the values of "*a*" calculated from the critical constants by its means were found to be nearly additive†, *e. g.*, the homologous increment was nearly constant in a given series. At the present stage the selection of this equation may be justified by the fact that, since the critical temperature is proportional to $\frac{a}{b^{2/3}}$, the doubling of *a* and *b* by association leads to a higher critical temperature, a conclusion which is more in accordance with the facts than that deduced from van der Waals's equation.

In equation (1) *V* represents the volume of a gram molecule. If the substance is associated the size of the molecule is not known, but we may substitute $n_c V$ for *V* and define *V* as the volume of a gram formula weight, n_c being the association factor at the critical point. Solving for n_c we get

$$n_c = \frac{4}{15} \frac{RT_c}{P_c V_c} \cdot . \quad . \quad . \quad . \quad . \quad (2)$$

* See Ostwald's *Handbuch der Allgemeinen Chemie*, vol. iii. p. 344.

† H. van Laar finds that *b* and \sqrt{a} determined from the critical constants by van der Waals's equation are approximately additive. These relationships are not sufficiently accurate for the purpose of the present investigation. *Journ. Chem. Phys.* xiv. p. 3; xvi. p. 411; xviii. p. 273.

But the critical coefficient $\frac{RT_c^*}{P_c V_c}$ is not quite constant even for substances such as the paraffins, which are usually considered to be unassociated so that $n_c=1$. Guye and Walden both regard this critical coefficient as a function of the critical temperature, but the present author finds that it can be represented much more accurately as a function of the length of the molecule. Thus, for instance, the critical coefficient of di-iso-butyl is (3·810), a value closer to that for hexane (3·83), which has the same length of molecule, than to that for octane (3·865), with which it is isomeric. The critical coefficients of isopentane (3·735) and di-isopropyl (3·741), which have the same length of molecule, are almost equal and smaller than the value for pentane (3·766). Very short molecules, such as methane (3·46) and hydrogen (3·27), have correspondingly small critical coefficients. These relationships are almost entirely obscured if we regard this critical coefficient as a function of the critical temperature.

If in equation (1) we introduce a function of the length “ l ” of the molecule thus :

$$\left(P + \frac{a}{(n_c V)^{5/3}}\right)(n_c V - b) = RT \times \frac{1}{f(l)}, \quad \dots (3)$$

we get for “ n_c ”

$$n_c = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \quad \dots (4)$$

where $f(l) = 0\cdot838 + 0\cdot174 \log l$.

This function of “ l ” has been so chosen that “ n_c ” is as nearly as possible unity for the saturated paraffins.

The length of the molecule is estimated by means of a few simple conventions from the following atomic diameters :—

Hydrogen	0·75
Oxygen	1·30
Nitrogen	1·30
Carbon.....	1·54
Fluorine	1·35
Chlorine	2·10
Bromine	2·38
Iodine	2·80
Tin	2·80

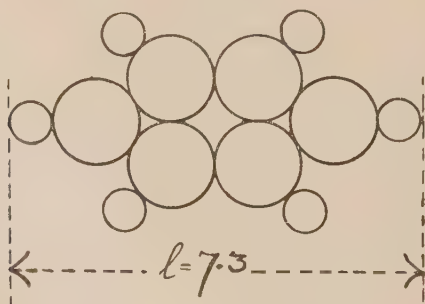
With the exception of hydrogen these are the usually accepted atomic diameters. Further research and a more

* S. Young correlated abnormal values of this quantity and molecular association, and the relationship has been generally accepted.

accurate evaluation of $f(l)$ may render it possible to use the normal atomic diameter of this element. The length of a molecule is taken as the sum of the atomic diameters in the longest chain, shorter side chains being neglected entirely. The molecules are therefore regarded as being stretched out to their greatest length, no account being taken of zig-zag or spiral formations. In this way we get the following values of " l ":—

Methane	1 carbon atom + 2 hydrogen atoms	$l=3.04$
Butane	4 carbon atoms + 2 hydrogen atoms	$l=7.66$
Pentane	5 carbon atoms + 2 hydrogen atoms	$l=9.20$
Iso-pentane	4 carbon atoms + 2 hydrogen atoms	$l=7.66$
Ethyl alcohol	2 carbon atoms + 2 hydrogen atoms	$l=5.88$
	+ 1 oxygen atom	

This convention breaks down when estimating the length of molecules containing a ring structure. It is found, however, that in order to make " n_c " equal to unity for the saturated ring compound hexamethylene one must assume a length of 7.3. This is in accordance with spatial considerations, if we assume that the ring is stretched out to its greatest length, as in the case of straight chain molecules. The ring might be pictured thus:—



This conception indicates that meta- and ortho-di-derivatives will be shorter than the corresponding para-di-derivative.

It seems reasonable to suppose that when two molecules associate to form one, the double molecule thus formed will have twice the length of the single molecule. Ordinary chemical considerations, supported by the work of Langmuir and others on surface films, suggest that in the case of primary substitution products the point of attachment would be the terminal group. If this is so, the average length of

the molecule of an associated substance will be greater than that found by the conventional method just described. One might get over this difficulty by substituting $n \times l$ for l in equation (4), but this leads to an expression which is difficult to solve. The correction is in any case small, and one may use the following approximation:—

$$n_c^{1+x} = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \quad . \quad . \quad . \quad (4a)$$

$\log \frac{f(2l)}{f(l)}$

where x is equal to $\frac{\log \frac{f(2l)}{f(l)}}{\log 2}$. This gives accurate results when $n=1$ and when $n=2$. For intermediate values of n it is a satisfactory approximation. It could not be used if n_c were appreciably greater than 2, but no association factor greater than 1.5 has been found at the critical point up to the present.

Values of n_c calculated from (4a) are recorded in Table I. Values of $\frac{4}{15} \frac{RT_c}{P_c V_c}$ are given for comparison in order to show just what influence the introduction of $f(l)$ into the expression exerts on the values of " n_c ". Deviations from unity in the case of normal saturated paraffins may be regarded as due to inaccuracies in the evaluation of $f(l)$. It is not maintained that the saturated paraffins are absolutely free from double molecules, but it is believed that they are at most only very slightly associated. The method adopted here is to determine the association factor of an organic compound in terms of that of a saturated paraffin having the same length of molecule. The basis of the method rests, therefore, on the carbon skeleton, and it must be applied with caution to purely inorganic substances. On the other hand, the association factors calculated for the inorganic substances hydrogen, oxygen, nitrogen, water, ammonia, hydrogen chloride, and stannic chloride appear to be reasonable and in accordance with what one might expect from the general properties of these substances. The results recorded in the table will be discussed in another communication, when the association factors have been determined at temperatures other than the critical. It may be pointed out, however, that the results are in general agreement with those given by Guye's molecular refraction method, but are free from certain anomalies which indicate that Guye's method is not reliable.

TABLE I.

Substance.	<i>l.</i>	$\frac{4}{15} \frac{RT_c}{P_c V_c}$	<i>n_c.</i>
Hydrogen	1.5	0.872	1.003
Oxygen	2.6	0.912	1.002
Nitrogen	2.6	0.912	1.002
Carbon dioxide	4.14	0.957	1.012
Methane	3.04	0.923	1.001
Ethane	4.58	0.947	0.994
Pentane	9.20	1.004	0.998
Hexane	10.74	1.022	1.005
Heptane ..	12.28	1.028	1.000
Octane	13.82	1.031	0.995
Iso-pentane	7.56	0.996	1.005
Di-iso-propyl	7.56	0.998	1.007
Di-iso-butyl	10.74	1.016	0.999
Methyl formate	6.43	1.046	1.062
Ethyl „	7.97	1.039	1.041
Propyl „	9.51	1.032	1.022
Methyl acetate	7.42	1.051	1.057
Ethyl „	8.96	1.053	1.046
Propyl „	10.50	1.049	1.031
Methyl propionate	8.96	1.042	1.035
Ethyl „	10.50	1.046	1.028
Methyl butyrate	10.50	1.041	1.023
„ iso-butyrate	8.96	1.031	1.025
Ethyl ether	8.96	1.017	1.012
Benzene	7.30	1.001	1.012
Fluorbenzene	7.90	1.012	1.017
Chlorbenzene	8.65	1.007	1.006
Brombenzene	8.93	1.016	1.012
Iodobenzene	9.35	1.008	1.001
Methyl chloride	4.39	1.016	1.065
Carbon tetrachloride	5.74	0.981	1.010
Tin tetrachloride ..	7.00	0.997	1.011
Methyl alcohol	4.34	1.216	1.259
Ethyl „	5.88	1.074	1.097
Propyl „	7.42	1.066	1.072
Acetic acid	5.88	1.332	1.341
Acetonitrile	5.13	1.452	1.470
Propionitrile	6.67	1.306	1.305
Water	2.80	1.189	1.270
Ammonia	2.80	1.020	1.091
Hydrogen chloride	2.85	0.973	1.057

It is interesting to note that the expression

$$n_c = \frac{4}{15} \frac{RT_c}{P_c \bar{V}_c},$$

uncorrected for the influence of the length of the molecule, indicates that the permanent gases are dissociated, whilst Guye's molecular refraction method indicates that they are associated. The method described in this paper indicates that they are normal substances, and this is probably the truth.

Summary.

It has been shown that the critical coefficient $\frac{RT_c}{P_c \bar{V}_c}$ is a function of the length of the molecule in the case of the saturated paraffins and certain other normal substances. Making use of this relationship the association factors of forty-one substances at the critical point have been calculated. The values thus obtained are rational and in accordance with what might be expected from the general properties of these substances.

PART II.—THE INFLUENCE OF MOLECULAR ASSOCIATION ON THE CRITICAL CONSTANTS.

It has been shown in Part I. that the equation

$$\left(P + \frac{a}{(n_c \bar{V})^{5/3}}\right)(n_c \bar{V} - b) = RT \times \frac{1}{f(l)} \quad . \quad . \quad (3)$$

is very nearly accurate at the critical point. It would be possible, therefore, by means of this equation to calculate the influence of the association factor n_c on the critical constants, if its influence on the constants " a ," " b ," and " l " were known. The influence of molecular association on " l " has been discussed in Part I. If the molecular attractive power " a " and the molecular volume " b " were strictly additive quantities their values for double molecules would be $2a$ and $2b$. In actual fact they are nearly additive in non-associated homologous series, but " b " in particular shows marked irregularities in the case of very small molecules such as hydrogen and methane. Le Bas has discussed these irregularities*, which are equally noticeable in the

* G. le Bas, 'The Molecular Association of Liquid Chemical Compounds,' pp. 24 & 124, 1915 (Longmans, Green, & Co.). The author's views on this matter are rather complex.

molecular volumes at the boiling-point, and he appears to regard these divergences from the additive law as functions of the molecular volume. The present author finds that they can be represented as a function of the molecular length, and though the evidence at present available is insufficient to enable one to decide on the relative merits of these two views, the latter has been adopted for the sake of convenience. This correction is very small except in the case of small molecules, such as methane and hydrogen. This is illustrated by the values in Table I., where the correction factors calculated from the functions of " l " are tabulated. The correction for hydrogen is very nearly 250 per cent., that for methane is 22 per cent., and for the remainder it is small. The molecular attraction constant " α " is so nearly additive that very little alteration is needed, but such divergences as there are can be corrected for quite satisfactorily by an empirical function of " l ." Thus for " α " and " b " in equation (3), one may substitute the following expressions:—

$$\begin{aligned} a &= \alpha \times [f(l)]^{2.3}, \\ b &= \beta \times f(l) \times f'(l), \end{aligned}$$

where $f(l) = 0.838 + 0.174 \log l$ (as in equation (3))

and $f'(l) = 1 \times \frac{12.2}{l^3}$.

These expressions are constants for a given substance and do not therefore affect the validity of the equation, and since " α " and " β " are now very nearly additive it is possible to write 2α and 2β for double molecules. If the theory of mixtures were followed exactly very complicated expressions would ensue, but the errors introduced by writing $n \times \alpha$, $n \times \beta$, and $n \times l$ for an associated substance would be small; thus equation (1) becomes

$$\begin{aligned} \left(P + \frac{n^{1+\frac{2}{3}x} \times \alpha \times [f(l)]^{2/3}}{(nV)} \right) (nV - n^{1+x+y} \times \beta \times (f(l))(f'(l))) \\ = \frac{RT}{n^x \times f(l)}, \quad \dots \quad (5) \end{aligned}$$

where V = volume of a gram formula weight,

n = association factor,

$$x = \frac{\log \frac{f(2l)}{f(l)}}{\log 2}, \quad y = \frac{\log \frac{f'(2l)}{f'(l)}}{\log 2},$$

in which the approximation for $f(nl)$, suggested in Part I., p. 115, is made use of.

Solving this equation for the critical point, we get

$$n_c^{1+x} = \frac{4}{15} \frac{RT_c}{P_c V_c} \times \frac{1}{f(l)}, \dots \dots \dots (6)$$

$$\alpha = 4 \times \left(\frac{4}{15}\right)^{5/3} \times \frac{(RT_c)^{5/3}}{P_c^{2/3}} \times \frac{1}{n_c^{1+\frac{5}{3}x} [f(l)]^{7/3}}, \dots (7)$$

$$\beta = \frac{1}{15} \frac{RT_c}{P_c} \times \frac{1}{n_c^{1+2x+y} [f(l)]^2 \times f'(l)} \dots \dots (8)$$

Values of α and β for various saturated paraffins are recorded in Table II. In calculating these values it has been assumed that " n_c " is equal to unity. Values of $\Sigma\alpha_a$ and $\Sigma\beta_a$ calculated by summation of the following atomic values,

	α_a	β_a
Hydrogen	0.30	.00235
Carbon	2.99	.00940

are recorded for comparison, and indicate that α and β are approximately additive so far as the saturated paraffins are concerned. Here it may be noted that Le Bas has been followed in that a volume has been assigned to carbon which is equal to four times that of hydrogen. Less satisfactory results are obtained if a ratio of one to two is employed, the value for elementary hydrogen being particularly unsatisfactory and different from the value which it has in the hydrocarbons. The manner in which the functions of " l " (the values of which are also tabulated) contribute to the additive nature of α and β can be appreciated only after a careful study of Table II. For example, the values of α for

TABLE II.

	l	$[f(l)]^{1/3}$	α	$\Sigma\alpha_a$	$f'(l) \times [f(l)]^2$	β	$\Sigma\beta_a$
Hydrogen.....	1.5	.721	.55	.60	3.496	.0041	.0047
Methane	3.04	.827	4.09	4.19	1.219	.0187	.0188
Ethane	4.58	.894	7.93	7.78	1.024	.0333	.0329
Propane	6.12	.943	11.30	11.37	1.001	.0469	.0470
Butane	7.56	.979	14.96	14.96	1.011	.0612	.0611
Pentane	9.20	1.013	18.45	18.55	1.028	.0758	.0752
Hexane	10.74	1.041	22.28	22.14	1.046	.0898	.0893
Heptane	12.28	1.065	25.73	25.73	1.068	.1029	.1034
Octane	13.82	1.087	29.17	29.32	1.080	.1170	.1175
Iso-pentane	7.56	.979	18.76	18.55	1.011	.0758	.0752
Di-iso-propyl ...	7.56	.979	22.55	22.14	1.011	.0881	.0893
Di-iso-butyl	10.74	1.041	28.81	29.32	1.046	.1172	.1175

the isomers hexane and di-iso-propyl should be identical. They are 22.3 and 22.6 respectively, and thus differ by only one per cent. The values of the function of "*l*" differ by 6 per cent. Again, the values of β for the isomers octane and di-iso-butyl are practically identical, while the values of the corresponding functions of "*l*" differ by 3.5 per cent. In both these cases there would have been a divergence of several per cent. from the additive law but for the corrective influence of the functions of "*l*", which not only account satisfactorily for the influence of growing chains in normal saturated hydrocarbons, but also for certain isomeric rearrangements involving a change in the length of the molecule. The fact that β is additive for the early members of the paraffin series as well as for the later members has an important bearing on the question of molecular volumes, which will be dealt with at another time. It is not necessary for the present purpose that the values of α and β should be unchangeable for a given element and independent of environment. The fact that α_a for oxygen has a much smaller value in the esters than in the alcohols, and that α_a for hydrogen and carbon in the esters is slightly smaller than in the paraffins, is not a matter of great importance. All that is required is that atoms and groups shall retain their attractive power and volume unchanged so long as no serious change in chemical constitution is involved.

Values of α and β have been calculated for the various esters examined by Young, and these are recorded in Table III. Values of $\Sigma\alpha_a$ and $\Sigma\beta_a$ are recorded for comparison, and have been calculated from the following values :—

	α_a .	β_a .
Hydrogen26	.00231
Carbon	3.14	.00928
$\begin{array}{c} \text{O} \\ \\ \text{—C—O—} \end{array}$	6.52	.0231

The values of α_a found for carbon and hydrogen are smaller than the corresponding values for the paraffin hydrocarbons, but the values of β_a are practically the same. The general concordance between α and β and the corresponding quantities calculated by summation of the atomic and group values demonstrates their essentially additive nature. A

TABLE III.

	l_c	n_c	α	$\Sigma\alpha_a$	β	$\Sigma\beta_a$
Methyl formate	6.43	1.062	13.36	13.32	.0420	.0417
Ethyl ,, 	7.97	1.041	16.55	16.46	.0561	.0556
Propyl ,, 	9.51	1.022	19.98	19.60	.0695	.0695
Methyl acetate	7.42	1.057	16.49	16.46	.0558	.0556
Ethyl ,, 	8.96	1.046	19.44	19.60	.0699	.0695
Propyl ,, 	10.50	1.031	22.81	22.74	.0838	.0834
Methyl propionate	8.96	1.035	19.59	19.60	.0689	.0695
Ethyl ,, 	10.50	1.028	22.65	22.74	.0836	.0834
Methyl butyrate	10.50	1.023	22.73	22.74	.0826	.0834
Methyl iso-butyrate	8.96	1.025	22.66	22.74	.0829	.0834

more searching proof of the validity of equation (5) for associated substances would be to show that α and β retain their additive character for series of highly associated substances, such as the alcohols and nitriles. Unfortunately, full data are available only for a few substances out of these two series. Table IV. shows that if the effect of association

TABLE IV.

	α'	Δ for CH_2	β'	Δ for CH_2
Methyl alcohol	14.0		.0346	
Ethyl ,, 	15.4	1.4	.0448	.0102
Propyl ,, 	18.4	3.0	.0581	.0133
Acetonitrile.....	20.7		.0618	
Propionitrile	22.1	1.4	.0742	.0124
Butyronitrile	23.2	1.1	.0838	.0096
Capronitrile	30.0	3.4×2	.0995	$.0078 \times 2$

is neglected, the value of " n_c " being taken as unity, the values of α' and β' thus obtained are far from being additive quantities, the differences for the homologous increment being abnormal and variable. When the association factors calculated in Part I. are employed these anomalies disappear. The true values of α and β cannot be calculated in the case of butyro- and capronitrile, since the critical volumes of these substances have not been measured, but the true values of the remaining five substances, together with those

TABLE V.

	<i>l.</i>	<i>n_c.</i>	<i>α.</i>	Δ for CH ₂ .	<i>β.</i>	Δ for CH ₂ .
Methyl alcohol	4.34	1.259	10.48		.0276	
Ethyl ,, 	5.88	1.097	13.83	3.35	.0405	.0129
Propyl ,, 	7.42	1.072	16.90	3.07	.0537	.0132
Acetonitrile	5.13	1.470	13.14		.0413	
Propionitrile	6.67	1.305	16.76	3.62	.0531	.0118
Acetic acid.....	5.88	1.341	14.69		.0415	

for acetic acid, are recorded in Table V. The anomalies remarked in Table IV. have disappeared. The differences for the homologous increment are more nearly normal, and in the case of the alcohols the values of these increments do not differ much from one another. The value of β for acetic acid is very nearly the same as that for the isomeric methyl formate. The value of α is higher than that for methyl formate, but this is not surprising, since it is found that hydroxyl oxygen has a greater attractive power than oxygen in any other form. A comparison of the values of α and β for ethyl ether with those for the alcohols yields similar results. α_a for etheric oxygen is much less than for hydroxyl oxygen, while β_a is practically the same in both cases. All these facts taken together give support to the view that equation (5) represents the relationship between the critical constants and the association factor with some approach to accuracy. It should be possible, therefore, by means of this equation to determine the influence of molecular association on the three critical constants.

Solving equation (5) for temperature, pressure, and volume at the critical point, we get

$$T_c = \frac{15}{4^{8/3} \times R} \times \frac{\alpha}{\beta^{2/3}} \times f(l) f'(l)^{-2/3} \times n_c^{\frac{4}{3} + x - \frac{2}{3}y}, \quad (9)$$


$$P_c = \frac{1}{4^{8/3}} \times \frac{\alpha}{\beta^{5/3}} \times f(l) f'(l)^{-5/3} \times n_c^{-\frac{2}{3} - x - \frac{2}{3}y}, \quad (10)$$

$$V_c = 4\beta \times f(l) f'(l) \times n_c^{x+y}. \quad (11)$$

From these three expressions the influence of the association factor on the critical constants can be determined. Unfortunately, the validity of these derived equations cannot be proved by direct observation, since up to the present no one has succeeded in determining the critical constants of a sub-

stance in any state of association other than that which is natural at the critical point, though Baker's experiments on very carefully dried substances indicate the possibility that this may be achieved eventually. It is possible, however, to compare the critical constants of pairs of substances such as benzene and diphenyl, and to see if these are in agreement with equations (9), (10), and (11). Diphenyl is slightly less than twice a benzene molecule, accordingly neither α nor β nor l is exactly doubled. Thus, for example, when two molecules of benzene are joined together with the elimination of two atoms of hydrogen to form a molecule of diphenyl, $\Sigma\alpha$ is increased 1.970 times, $\Sigma\beta$ is increased 1.933 times, and " l " is increased from 7.3 to 13.1 (*i. e.*, $2 \times [7.3 - 0.75]$). From these data one can calculate the effect of thus nearly doubling the size of the molecule on the critical constants of benzene on the assumption that n_c (which, in the case of hydrocarbons, differs but little from unity) remains constant, by means of equations (9), (10), and (11). The results of these calculations for the critical temperature and the critical pressure are given in Table VI.

TABLE VI.

Substance.	Ratio of	Ratio of
	Critical Temperatures.	Critical Pressures.
	$\frac{T_c \text{ double molecule}}{T_c \text{ single molecule}}$	$\frac{P_c \text{ double molecule}}{P_c \text{ single molecule}}$
H_3C-CH_3	1.55 (1.60)	1.06 (1.07)
$H_3C_2-C_2H_5$	1.41 (1.39)	0.766 (0.769)
$H_7C_3-C_3H_7$	1.37 (1.37)	0.686 (0.686)
$H_9C_4-C_4H_9$	1.33 (1.34)	0.656 (0.657)
	1.38 (1.37)	0.666 (0.663)
$H_2C : H_3C_2 - C_2H_3 : CH_2$	1.37 (1.37)	0.692 —
$H_2C : H_7C_4 - C_4H_7 : CH_2$	1.34 (1.30)	0.640 —

Observed values are printed in parentheses.

together with similar calculations for six other hydrocarbons, and the observed values for these substances calculated from

the actual critical data. From these values it is seen that the critical temperature is always increased by doubling the size of the molecule, and that the critical pressure, though usually reduced under these circumstances, is in the case of methane (a short molecule) actually increased. Reliable experimental data for checking the calculated critical volume ratios are not to be found in the literature; these are therefore omitted from the table. It may be stated, however, that they are in general agreement with the ratios calculated from the molecular volumes at the boiling-point. The calculated critical temperature and critical pressure ratios are in very good agreement with those found by experiment. It is therefore reasonable to conclude that equations (9), (10), and (11) are in accordance with the facts, and that it is possible by means of them to determine the influence of molecular association on the critical constants.

The question now arises as to the exact physical meaning of the constants α and β . Equation (5) has been derived from van der Waals's equation by means of empirical modifications introduced in order

- (a) to make the equation reasonably accurate at the critical point;
- (b) to make the constants additive in order that one might write $n\alpha$ and $n\beta$ for an associated substance.

One cannot, therefore, be sure that α and β represent accurately the molecular attractive power and the molecular volume respectively. There is much evidence, including that afforded by molecular refraction, to show that the space occupied by the molecules is additive with respect to the atoms and atomic groups of which the molecule is built up. It is, moreover, intrinsically probable that both the volume of the molecule and the molecular attractive power should be additive in the limited sense suggested in this paper. It therefore seems probable that α and β may be more closely proportional to the true values of the physical properties they claim to represent than " a " and " b " determined from the critical constants by the theoretically derived equation of van der Waals.

An absolutely independent method* of measuring the molecular attractive power of substances in solution was devised by H. E. Armstrong and the present author, and it was found that this quantity was approximately additive. This molecular attractive power was estimated from the

* Proc. Roy. Soc. A, lxxxix, p. 375 (1914).

effect of the substance on the rotatory power of fructose in aqueous solution by means of the expression

$$A = \frac{1}{M} (0.037 \Delta V - \Delta[\alpha]),$$

where A = molecular attractive power of solute,

M = molecular proportions of solute added,

ΔV = increase in volume produced by the addition of the solute,

$\Delta[\alpha]$ = change in rotatory power of the fructose in solution.

From this expression values of the molecular attractive power were calculated, and from these values atomic values were deduced. These are given below, together with the relative values of α_a :—

Atom or Group.	A_a .	$0.085 \alpha_a$.
—H	negligible	·026
>CH ₂	0.23	·267
—OH	0.70	·616
—C : N	0.74 *	·788

The parallelism between the two sets of values gives some support to the view that both A and α are measures of the molecular attractive power. It should be pointed out, however, that, for the purpose of the argument put forward in this paper, it is not absolutely necessary that α , β , and l should represent accurately the molecular attractive power, the molecular volume, and the molecular length. Equation (5) may be regarded as an empirical relationship between the critical constants containing the three quantities α , β , and l , which are found to be additive in the sense that they become approximately $n\alpha$, $n\beta$, and nl when the substance is associated n -fold.

Summary.

It has been shown that the constants α and β in a modified equation of state are additive quantities, both in the case of associated and unassociated substances. By means of this equation the effect on the critical constants of doubling the

* This is not the value given in the paper referred to, but it is that which is obtained if the same equation is used as that employed for the other two values. A less accurate expression was used in the paper, which neglected the influence of the homologous increment.

size of the molecule can be calculated, and the results of these calculations are in good agreement with existing experimental data. From this it is concluded that the modified equation of state is suitable for calculating the effect of molecular association on the critical constants.

In the next paper it will be shown how a knowledge of the manner in which the critical constants are affected by the degree of association can be used to calculate the association factor of liquids at various temperatures.

The author desires to thank Professor Lowry for his helpful criticism of these papers.

XI. *On the Effect of Aural Fatigue upon the Critical Frequency of Pulsation of Tones.* By MOLLIE WEINBERG, M.A., M.Sc., Research Student of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, and FRANK ALLEN, Ph D., F.R.S.C., Professor of Physics, University of Manitoba*.

THIS investigation is concerned with the effects of fatigue upon the persistence of audition, or the duration of the tone at the critical frequency of pulsation or flutter. The results herein described seem to throw new light upon some of the phenomena of acoustics, and also upon the probable structure of the aural mechanism by means of which tones are perceived and differentiated from each other.

The apparatus used is the same as that described in a previous communication†.

The source of sound was a tonvariator blown by a stream of air from a constant-pressure tank. The tonvariator was enclosed in a sound-proof box having one opening through which the sound could escape. The periodic interruption of the continuous sound was effected by the rotation of an aluminium disk in which were four holes of the same size as that of the opening in the box. For measuring the time of rotation of the disk, a speed counter and a clock beating half-seconds were electrically connected to a chronograph. When making measurements, the speed of the disk was adjusted so that the pulsation or flutter of the sound became just imperceptible, and then recorded. For fatiguing the

* Communicated by the Authors. Read at the meeting of the Royal Society of Canada, Ottawa, May 1922.

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

ear, another tonvariator similar in all respects to the one in the sound-proof box, was used. Both instruments were calibrated from Standard Tuning Forks.

An attempt was made to determine the progressive effect of fatigue for increasing intervals of time, but the results were too uncertain to be of much use. The maximum fatigue seemed, however, to be attained in about two minutes for low intensities of sound. In the following experiments this interval of time was therefore allowed for fatiguing the ear before each measurement was made.

Two methods were used in this part of the work, one the converse of the other, in the hope that the results obtained from one would confirm those obtained from the other. Such happily appeared to be the case.

The first method consisted in fatiguing the ear with a tone of constant frequency, and taking measurements on tones varying over a range of about fifteen vibrations above and the same number below the fatiguing tone. The second method consisted in taking measurements on a tone of constant frequency, and varying the fatiguing stimulus over a similar range of about thirty vibrations.

In making measurements the following procedure was adopted. At a definite blowing-pressure, the tonvariator in the box, upon which the measurements were made, was adjusted to give a tone of any desired pitch, and the second tonvariator was accurately tuned with it by means of eliminating beats. The left ear was then fatigued with this tone for two minutes by holding it close to the orifice of the tonvariator, and immediately afterwards the measurement of the critical frequency of pulsation or flutter of tone was made. The fatiguing process was again and again repeated, and similar measurements were made on a selected series of tones.

Sets of such measurements are given in Table I. The persistency curves defined by these points were taken to represent the effect produced by fatiguing the ear with tones of constant frequency. The curves are shown in fig. 1. The curve through the small circles is the normal obtained with the unfatigued ear, and is plotted from the data in Table VI., F, which is taken from a former communication*. The broken line curves through the x's are the fatigue curves. These are characterized by prominent elevations covering in each case a range of about sixteen vibrations, with the maximum occurring at the frequency of the fatiguing tone, as is to be expected.

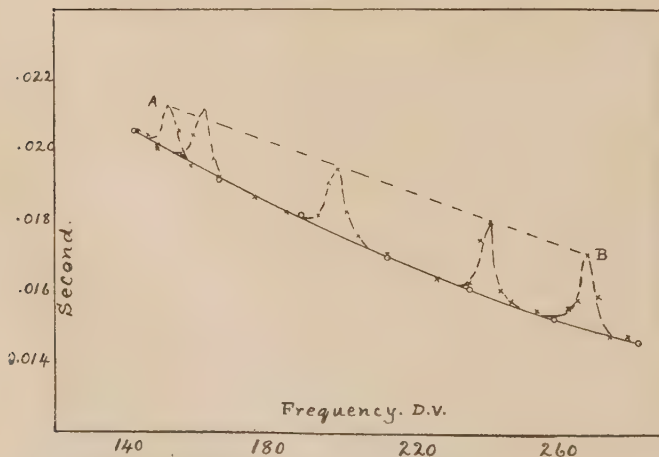
* "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

TABLE I.

Fatigue Curves for different Frequencies at same Pressure.

Pressure.	Frequency.	Duration.	Pressure.	Frequency.	Duration.
P.	N.	D.	P.	N.	D.
Normal Curve.			Fatigue Curves (cont.).		
	D.V.	Sec.		D.V.	Sec.
1.82 cm.	143.0	0.0206	1.82 cm.	149.0	0.0201
"	167.0	.0192	"	156.4	.0199
"	190.0	.0187	"	159.2	.0205
"	214.0	.0170	"	162.2	.0212
"	237.0	.0161	"	165.0	.0198
"	260.5	.0153	"	168.0	.0192
"	284.0	.0146	"	176.5	.0187
Fatigue Curves.					
1.82 cm.	133.0	0.0206	1.82 cm.	185.8	0.0183
"	146.0	.0205	"	194.5	.0182
"	149.5	.0202	"	197.2	.0191
"	152.5	.0213	"	200.0	.0195
"	155.5	.0206	"	202.8	.0183
"	158.2	.0196	"	205.6	.0176
"	167.0	.0193	"	213.8	.0171
1.82 cm.	227.8	0.0164	1.82 cm.	255.8	0.0155
"	237.0	.0163	"	264.0	.0156
"	240.0	.0175	"	267.0	.0158
"	242.8	.0180	"	269.6	.0171
"	245.5	.0161	"	272.4	.0159
"	248.2	.0158	"	275.2	.0148
"	255.8	.0155	"	281.0	.0148

Fig. 1.



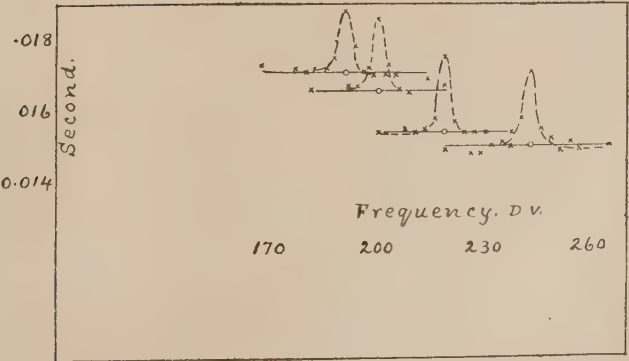
By the converse method, similar fatigue curves were obtained, the measurements being made, in each case, on a constant tone, and the fatiguing tone being varied over a range of about forty vibrations, as shown in Table II. These fatigue curves are plotted in fig. 2. The elevations in these

TABLE II.

Fatigue Curves—by Second Method (Constant Pressure).

P.	N'.	D. Sec.	P.	N'.	D. Sec.
Normal Point.			Normal Point.		
1.78 cm.	190.5	0.0171	1.78 cm.	218.0	0.0154
Fatigue Curve.			Fatigue Curve.		
1.78 cm.	167.0	0.0173	1.78 cm.	200.0	0.0154
"	176.6	.0172	"	207.1	.0155
"	179.3	.0171	"	210.0	.0154
"	182.0	.0172	"	212.7	.0155
"	185.0	.0172	"	215.7	.0158
"	187.5	.0175	"	218.4	.0175
"	190.5	.0188	"	221.3	.0157
"	193.2	.0178	"	224.0	.0154
"	196.0	.0171	"	226.6	.0154
"	198.5	.0170	"	229.8	.0154
"	201.7	.0170	"	237.1	.0154
"	204.5	.0170			
"	213.6	.0169			
Normal Point.			Normal Point.		
1.78 cm.	199.8	0.0166	1.78 cm.	244.8	0.0150
Fatigue Curve.			Fatigue Curve.		
1.78 cm.	181.0	0.0166	1.78 cm.	218.4	0.0149
"	191.2	.0167	"	226.0	.0148
"	194.0	.0167	"	228.7	.0148
"	196.9	.0172	"	231.6	.0150
"	199.8	.0186	"	234.5	.0151
"	202.6	.0173	"	237.0	.0150
"	205.3	.0166	"	240.0	.0157
"	208.1	.0165	"	242.8	.0171
"	218.4	.0167	"	245.5	.0155
			"	248.2	.0152
			"	251.0	.0149
			"	254.0	.0151
			"	256.8	.0149
			"	265.0.	.0150

Fig. 2.



curves are symmetrical with the axis of frequencies, since the normal has only one value, which is the duration of the tone on which measurements were made at the critical frequency of pulsation. This is indicated in each case by a small circle at the proper frequency, through which the full horizontal line is drawn. The elevations again are found to cover the same range of about sixteen vibrations.

In the tables, P is the blowing pressure, in centimetres of water, to which the intensity of the sound of the tonvariator is proportional* ; N is the frequency of vibration of the tonvariator ; and D is the duration of the tone at the critical frequency of pulsation, or flutter.

The curves indicate that as a result of fatigue the persistency of sound impressions is greatly increased. This increase is a maximum when the frequency of the fatiguing tone is the same as that upon which measurements are taken, and diminishes very rapidly as the interval from the frequency of the fatiguing tone is increased. The entire range affected is about sixteen vibrations, or about eight on each side of the maximum. The steepness of the slope indicates that only a few vibrations very near the maximum on both sides are affected to any great extent.

The general nature of the fatigue curve is seen to be the same for each frequency. It will be noticed, especially in fig. 1, that as the frequency is increased the height of the elevation also increases. So perfectly do they vary together, that in this figure the maxima of the elevations lie on a straight line, shown in the figure as the broken line AB. No doubt if the ear were exposed to sounds of considerable intensity for a couple of minutes while instrumental adjustments were being made, the apparently "normal" curve thereby obtained would in reality be the straight line forming the locus of the maxima of the fatigue elevations. Possibly this may have been the case in Mayer's experiments, and may explain why his normal curves were straight lines, as indicated in a former communication †.

The elevations also show a slight gradual widening of their bases as the frequency is increased. This would indicate that the range of resonance arches in the ear affected by any tone is slightly greater as the frequency is raised. The range of frequencies used in this investigation, consisting of

* Misses Love and Dawson, *Phys. Rev.* vol. xiv. p. 49 (1919).

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

but one octave, is, however, too small for any reliable conclusion to be drawn.

As indicated above, the elevations increase in height as the frequency of the fatiguing tone is increased. This may be caused by an increase in the sensitiveness of the resonating mechanism of the ear on account of pressure. In support of this idea an experiment due to Gelle may be cited. If a tuning-fork is pressed against the upper part of the forehead until its vibrations are faintly heard, and then a finger be pressed against the ear so as to increase the pressure on the membranes, the physiological intensity of the tone is greatly increased.

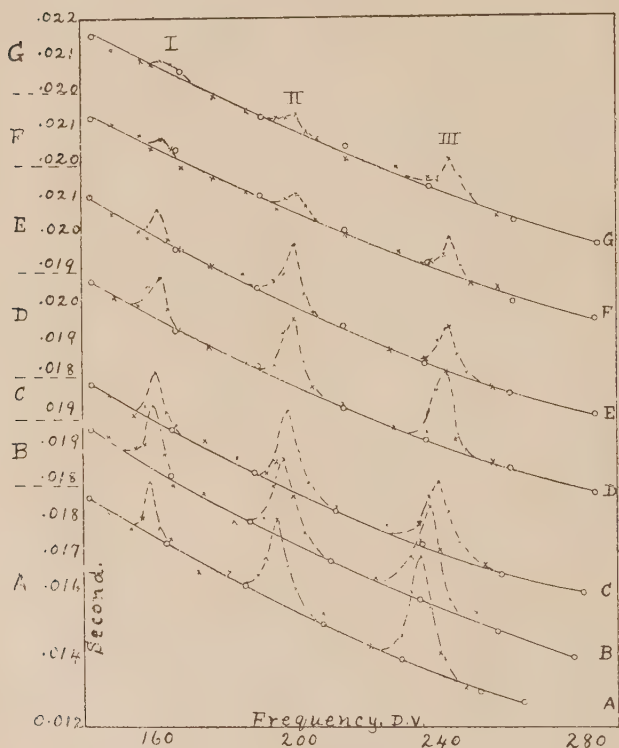
When the pitch of a tone is raised, the waves impinge upon the membranes of the ear with increasing frequency. The resonating arches may not therefore have sufficient time in which to recover from one impulse before the next wave arrives. The rising frequency of the tone may produce a certain steady increase of pressure, which, in turn, increases the sensitiveness of the auditory receptors. The resonating arches consequently are disproportionately fatigued and in such a condition respond more sluggishly to the stimulus, and the duration of the tone is increased when the frequency of pulsation reaches its critical value.

In fig. 3 are shown three (vertical) series of fatigue curves, each series representing the effect of fatigue of approximately the same frequency for seven different pressures or intensities. In series I. the fatiguing frequency was about 162, in series II. about 198, and in series III. about 240. The complete data are given in Table III. In examining this figure, it will be noticed that the lowest curve, A, is that for the lowest blowing-pressure, which gives the weakest tone, and the others represent tones gradually increasing in loudness. The curves are drawn to the same scale. The data for the normal curves are in Table VI. The columns N, in Table III., contain the tones upon which measurements were made.

The three series again show that the effect of fatigue is to increase the time of the critical frequency of pulsation. Also this increase becomes less as the intensity of the tone becomes greater. The diminutive size of the elevations in the curve G for the loudest tones employed indicates that for very intense sounds the fatigue elevations would disappear altogether. This might not be due, however, to the absence of fatigue, but to the probability that at higher intensities the ear is fatigued in much shorter time—that is, during the

time in which the measurements of the critical frequency of pulsation were being made. In that case, what would appear to be a smooth normal curve would in reality be the line through the maxima of a series of fatigue elevations as pointed out above. In fig. 3 the summits of the fatigue

Fig. 3.



elevations in the curves A, B, C, and D lie quite accurately on straight lines, and the remainder nearly so.

These curves are fully confirmed by others obtained by the second method—that is, by measuring the critical frequency of pulsation of a tone of constant frequency, the fatiguing tone being varied in pitch. The measurements are shown in Table IV, and the curves corresponding in fig. 4.

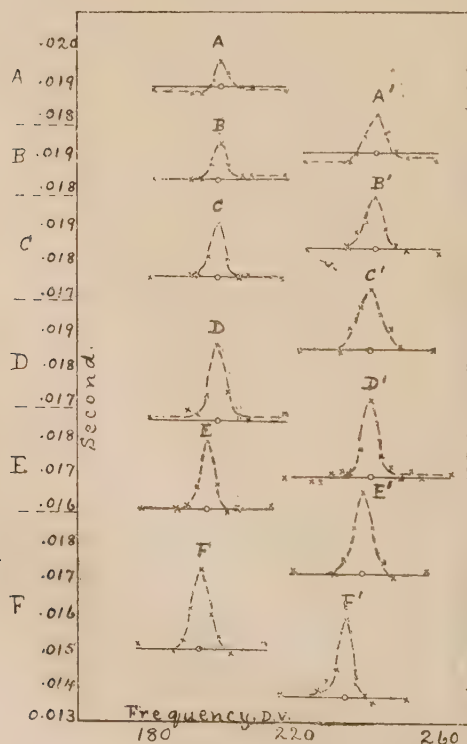
TABLE III.
Fatigue Curves. First Method.

N. D.		N. D.		N. D.	
I G.		II G.		III G.	
Press., 2.40 cm.		Press., 2.40 cm.		Press., 2.40 cm.	
Fatiguing Tone, 163.0.		Fatiguing Tone, 201.0.		Fatiguing Tone, 244.0.	
149.0	0.0211 sec.	186.7	0.0194 sec.	229.0	0.0178 sec.
157.2	.0208	195.2	.0193	238.4	.0175
160.0	.0207	198.0	.0193	241.2	.0174
163.0	.0208	201.0	.0193	244.0	.0180
165.9	.0207	203.8	.0188	247.0	.0175
168.0	.0204	206.7	.0186	249.8	.0170
177.2	.0198	215.0	.0180	257.0	.0164
I F.		II F.		III F.	
Press., 2.20 cm.		Press., 2.20 cm.		Press., 2.20 cm.	
Fatiguing Tone, 163.0.		Fatiguing Tone, 201.0.		Fatiguing Tone, 244.0.	
149.0	0.0210 sec.	186.7	0.0191 sec.	229.0	0.0174 sec.
157.2	.0207	195.2	.0186	238.4	.0171
160.0	.0203	198.0	.0189	242.2	.0173
163.0	.0206	201.0	.0190	244.0	.0178
165.9	.0203	203.8	.0187	247.0	.0170
168.8	.0198	206.7	.0183	249.8	.0165
177.2	.0195	215.0	.0179	257.0	.0164
I E.		II E.		III E.	
Press., 1.98 cm.		Press., 1.98 cm.		Press., 1.98 cm.	
Fatiguing Tone, 162.2.		Fatiguing Tone, 200.0.		Fatiguing Tone, 242.8.	
149.0	0.0205 sec.	185.8	0.0178 sec.	227.8	0.0167 sec.
156.4	.0200	194.5	.0176	237.0	.0163
159.2	.0198	197.2	.0178	240.0	.0169
162.2	.0206	200.0	.0186	242.8	.0173
165.0	.0198	202.8	.0172	245.5	.0165
168.0	.0195	205.6	.0167	248.2	.0160
176.5	.0190	213.8	.0163	255.8	.0156
I D.		II D.		III D.	
Press., 1.82 cm.		Press., 1.82 cm.		Press., 1.82 cm.	
Fatiguing Tone, 162.2.		Fatiguing Tone, 200.0.		Fatiguing Tone, 242.8.	
149.0	0.0201 sec.	185.8	0.0183 sec.	227.8	0.0164 sec.
156.4	.0199	194.5	.0182	237.0	.0163
159.2	.0205	197.2	.0191	240.0	.0175
162.2	.0207	200.0	.0195	242.8	.0180
165.0	.0198	202.8	.0183	245.5	.0161
168.0	.0192	205.6	.0176	248.2	.0158
176.5	.0187	213.8	.0171	255.8	.0155
I C.		II C.		III C.	
Press., 1.53 cm.		Press., 1.53 cm.		Press., 1.53 cm.	
Fatiguing Tone, 161.0.		Fatiguing Tone, 198.0.		Fatiguing Tone, 240.3.	
147.5	0.0194 sec.	184.0	0.0176 sec.	225.8	0.0157 sec.
155.0	.0188	192.3	.0172	235.0	.0157
158.0	.0191	195.0	.0175	237.6	.0165
161.0	.0200	198.0	.0189	240.3	.0169
163.9	.0189	200.8	.0178	243.0	.0161
166.6	.0185	203.5	.0169	246.0	.0152
175.0	.0181	211.8	.0162	253.0	.0146

TABLE III. (*contd.*).
Fatigue Curves. First Method.

N.	D.	N.	D.	N.	D.
I B.		II B.		III B.	
Press., 1.45 cm.		Press., 1.45 cm.		Press., 1.45 cm.	
Fatiguing Tone, 160.8.		Fatiguing Tone, 197.0.		Fatiguing Tone, 238.0.	
147.3	0.0192 sec.	183.0	0.0168 sec.	222.8	0.0152 sec.
155.2	.0189	191.2	.0169	232.4	.0158
158.0	.0190	194.0	.0178	235.2	.0162
160.8	.0201	197.0	.0186	238.0	.0172
163.6	.0187	199.8	.0175	240.8	.0160
166.0	.0178	202.5	.0165	243.6	.0146
174.3	.0176	210.0	.0158	251.0	.0142
I A.		II A.		III A.	
Press., 1.25 cm.		Press., 1.25 cm.		Press., 1.25 cm.	
Fatiguing Tone, 159.4.		Fatiguing Tone, 195.0.		Fatiguing Tone, 235.2.	
147.0	0.0181 sec.	181.8	0.0164 sec.	221.2	0.0143 sec.
154.0	.0176	189.6	.0163	230.0	.0146
156.9	.0179	192.0	.0168	232.7	.0158
159.4	.0189	195.0	.0179	235.2	.0168
162.0	.0176	197.6	.0165	238.0	.0154
165.0	.0173	200.0	.0159	240.6	.0141
173.0	.0164	208.0	.0152	247.8	.0131

Fig. 4.



In Table IV. the tones in the columns, N', were the fatiguing tones.

TABLE IV.
Fatigue Curves. Second Method.

N'.	D.	N'.	D.	N'.	D.	N'.	D.
A.		A'.		D.		D'.	
Press., 2.40 cm.		Press., 2.40 cm.		Press., 1.78 cm.		Press., 1.78 cm.	
Constant		Constant		Constant		Constant	
Tone, 201.0.		Tone, 244.0.		Tone, 199.8.		Tone, 242.8.	
182.0	0.0188	224.5	0.0168	181.0	0.0166	218.4	0.0149
192.5	.0187	235.8	.0168	191.2	.0168	226.0	.0148
195.2	.0187	238.4	.0170	194.0	.0167	228.7	.0148
198.0	.0191	241.2	.0175	196.9	.0172	231.6	.0150
201.0	.0196	244.0	.0181	199.8	.0186	234.5	.0151
203.8	.0193	247.0	.0176	202.6	.0173	237.0	.0151
206.7	.0189	249.8	.0171	205.3	.0166	240.0	.0157
209.5	.0189	252.8	.0169	208.1	.0165	242.8	.0171
219.0	.0188	261.0	.0168	218.4	.0167	245.5	.0155
						248.2	.0152
						251.0	.0149
						254.0	.0151
						256.8	.0149
						265.0	.0150
B.		B'.		E.		E'.	
Press., 2.10 cm.		Press., 2.10 cm.		Press., 1.50 cm.		Press., 1.50 cm.	
Constant		Constant		Constant		Constant	
Tone, 201.0.		Tone, 244.0.		Tone, 197.0.		Tone, 240.3.	
182.0	0.0183	225.0	0.0163	178.0	0.0160	221.0	0.0143
192.5	.0183	236.0	.0164	188.2	.0160	232.0	.0142
195.2	.0183	238.4	.0168	191.2	.0161	235.0	.0146
198.0	.0187	241.2	.0171	194.0	.0166	237.6	.0155
201.0	.0193	244.0	.0178	197.0	.0179	240.3	.0165
203.0	.0187	247.0	.0169	199.8	.0167	243.0	.0155
206.7	.0184	249.8	.0164	202.5	.0159	246.0	.0145
209.5	.0184	252.5	.0163	205.2	.0160	248.5	.0141
219.0	.0184	261.5	.0162	215.0	.0161	258.0	.0143
C.		C'.		F.		F'.	
Press., 1.98 cm.		Press., 1.98 cm.		Press., 1.16 cm.		Press., 1.16 cm.	
Constant		Constant		Constant		Constant	
Tone, 200.0.		Tone, 242.8.		Tone, 195.0.		Tone, 235.2.	
181.0	0.0175	223.0	0.0155	177.0	0.0152	217.0	0.0138
191.8	.0176	234.0	.0154	187.0	.0150	227.3	.0139
194.5	.0176	237.0	.0161	189.6	.0153	230.0	.0142
197.2	.0181	240.0	.0167	192.0	.0162	232.7	.0145
200.0	.0190	242.8	.0172	195.0	.0173	235.2	.0159
202.8	.0180	245.5	.0165	197.6	.0160	238.0	.0141
205.6	.0175	248.2	.0161	200.0	.0154	240.6	.0138
208.4	.0176	251.0	.0156	203.0	.0149	243.0	.0136
218.0	.0175	260.0	.0155	212.3	.0152	252.0	.0137

As in the preceding figures, the height of the elevations shows that the persistence after fatigue becomes greater as the musical scale is ascended. The narrowness of the range of

frequencies affected is seen more clearly in this figure because the reference curve or normal upon which the fatigue elevation is superimposed is the continuous horizontal line drawn through the normal value of the critical frequency of pulsation which is marked with a small circle.

In fig. 4, also, are shown two series of fatigue curves, each for a nearly constant frequency, but varying blowing-pressures or intensities. The lowest curves in the figure are for tones of weakest intensity. Again, the decrease in the apparent effect of fatigue as the tone increases in intensity is clearly indicated, as is also the increase in the effect of fatigue with increase of frequency—*i. e.*, the height of A' is greater than that of A , of B' than B , etc. The two methods therefore give results that are perfectly consistent with each other.

These results of aural fatigue are susceptible of explanation by assuming the existence of a resonance mechanism in the ear. We may suppose that the organ of Corti is that mechanism, the forty-five hundred arches acting as a series of resonators. For the sake of brevity, let us term those arches possessing natural vibration frequencies corresponding exactly to that of an entering wave the resonal arches of that frequency, and two or three adjacent arches on each side of the resonals the auxiliary arches. The evidence from the curves may be interpreted as follows. When a train of simple waves enters the cochlea, the resonal arches are set into vibrations of corresponding amplitude. The auxiliary arches are also quite strongly affected. Further, the arches corresponding to about five or six additional vibrations on each side of the resonals are also rhythmically disturbed, but the amount to which they are affected very rapidly diminishes as their distance from the resonals increases. If the ordinates of the fatigue elevation may be considered to represent the relative amplitudes of the vibrating arches, the intensities of the tones from the resonals and the auxiliary arches will be very great compared with those from the more distant arches, which will thereby become negligible. The mainly effective vibrations may therefore be considered to be those of the resonal and auxiliary arches.

But since the natural periods of vibrations of the auxiliary arches differ from each other as well as from the resonals, it would apparently follow that a single train of waves would produce perceptible tones of about five different frequencies. In the octave under study, these tones would differ from each other in the extreme by about the interval of a comma, 81/80, which is near the usual limit of perceptible difference

in pitch. But the various arches vibrating in their natural periods would produce a series of beats which would be easily, as well as annoyingly, perceived.

This general objection, though urged by Watt* against the Helmholtz resonance theory, is removed by Helmholtz himself †. "An elastic body set into sympathetic vibrations by any tone vibrates sympathetically in the pitch number of the exciting tone; but as soon as the exciting tone ceases, it goes on sounding in the pitch number of its own proper tone. This fact, which is derived from theory, may be perfectly verified on tuning-forks by means of the vibration microscope."

This conclusion, applied to the present experimental results, indicates that the reason why the auxiliary arches are not heard in their natural frequencies is because they are constrained to vibrate with the same frequency as the resonals. As soon as the exciting tone ceases, the entire range affected also ceases to vibrate; the tones due to the natural frequencies of the auxiliaries are therefore not heard. The high degree of damping experienced by the vibrating arches immersed in the lymph of the cochlea quite naturally prevents any continuance of vibration after the exciting wave-train ceases to act.

The main objection of Watt to a resonance theory is that the arches on each side of the resonals do not give experiences in conformity with the law of specific energies of sense. Watt may have been justified in his criticism since, according to Helmholtz ‡ himself, the effect of an exciting tone was distinguishable on the resonating arches responding to a range of two whole equally-tempered tones; that is, in the octave we are considering, about sixty-four vibrations. Helmholtz's curve is reproduced in fig. 5 in comparison with the fatigue curve of the tone of frequency 242.8, the measurements of the critical frequency of pulsation being made on a series of tones ranging from 218.4 to 265 vibrations, and the blowing-pressure being 1.78 cm. The data for the fatigue curve are given in Table V. The resonating arches disturbed, according to Helmholtz's curve, extend over a range more than four times as great as that indicated by the fatigue experiment. In estimating the data for his curve, Helmholtz states that exactness is out of the question. The method of the critical frequency of pulsation

* Watt, 'Psychology of Sound,' p. 142, 1917.

† Helmholtz, 'Sensations of Tone,' p. 144.

‡ *Loc. cit.*

combined with fatigue, however, enables measurements to be made with quite conclusive accuracy. The sharp-peaked character of the elevation of the fatigue curves, together with the very restricted range of frequencies disturbed, seem sufficient to remove from the resonance theory the objection urged by Watt.

Fig. 5.

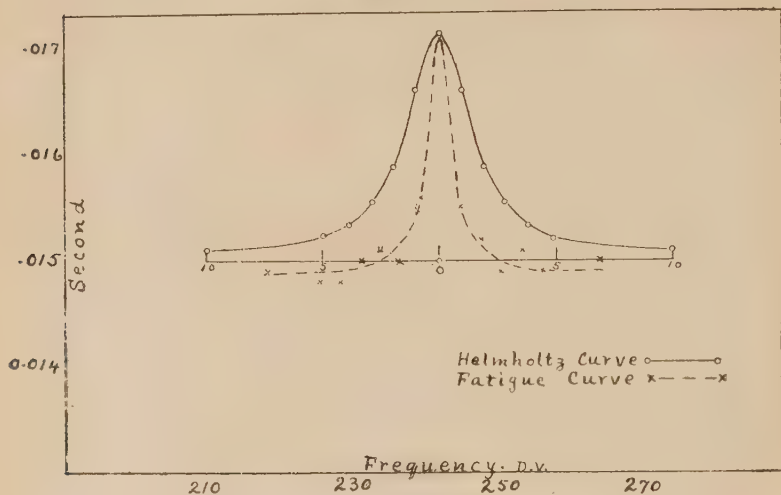


TABLE V.

Comparison of Helmholtz's Intensity Curve with Fatigue Curve.

P.	N'.	N.	D. Sec.
B. 1.78 cm.	218.4	242.8	0.0148
"	226.0	"	.0148
"	228.7	"	.0148
"	231.6	"	.0150
"	234.5	"	.0151
"	237.0	"	.0150
"	240.0	"	.0156
"	242.8	"	.0171
"	245.5	"	.0155
"	248.2	"	.0152
"	251.0	"	.0149
"	254.0	"	.0151
"	256.8	"	.0149
"	265.0	"	.0150

A. Helmholtz's Curve plotted from data in 'Sensations of Tone,' p. 144.

As pointed out above, the experiments herein described are limited to the octave from 142 to 284 vibrations. If the

character of the fatigue curves is the same in the octaves below as well as above, we can explain a well-known phenomenon in music.

It is universally recognized that shakes and runs in the bass are not clear, but that the tones merge into each other. This is independent of the instrument upon which they are played. Helmholtz * explains this as follows:—" Since the difficulty of shaking in the bass is the same for all instruments : and for individual instruments is demonstrably

TABLE VI.
Normal Curves.

Frequency. N.	Duration. D. Sec.	Pressure. P.	Frequency. N.	Duration. D. Sec.	Pressure. P.
A. 142.0	0.0185	1.25 cm.	F. 143.0	0.0206	1.82 cm.
164.0	.0172	"	167.0	.0192	"
186.0	.0160	"	190.0	.0182	"
208.0	.0149	"	214.0	.0170	"
230.0	.0139	"	237.0	.0161	"
252.0	.0130	"	260.5	.0153	"
264.0	.0127	"	284.0	.0146	"
B. 142.5	0.0194	1.45 cm.	G. 143.0	0.0210	1.98 cm.
165.5	.0181	"	167.0	.0195	"
187.5	.0168	"	190.0	.0184	"
210.0	.0157	"	214.0	.0173	"
235.0	.0146	"	237.0	.0163	"
256.7	.0137	"	260.5	.0154	"
278.0	.0130	"	284.0	.0148	"
C. 142.8	0.0197	1.53 cm.	H. 143.0	0.0211	2.10 cm.
165.8	.0184	"	167.2	.0200	"
188.8	.0172	"	190.2	.0187	"
211.8	.0161	"	214.2	.0177	"
235.7	.0152	"	237.2	.0166	"
257.9	.0143	"	260.7	.0158	"
280.5	.0138	"	284.2	.0151	"
D. 142.9	0.0201	1.62 cm.	I. 143.2	0.0212	2.20 cm.
166.2	.0187	"	167.3	.0203	"
189.0	.0177	"	191.0	.0190	"
212.0	.0166	"	214.6	.0180	"
235.3	.0155	"	238.0	.0171	"
258.2	.0146	"	261.2	.0160	"
280.9	.0140	"	284.2	.0155	"
E. 143.0	0.0203	1.70 cm.	J. 143.5	0.0215	2.40 cm.
166.6	.0190	"	168.2	.0205	"
189.7	.0179	"	191.2	.0192	"
213.2	.0168	"	215.0	.0184	"
236.2	.0158	"	238.3	.0173	"
259.3	.0149	"	261.9	.0163	"
283.0	.0143	"	285.0	.0156	"

* 'Sensations of Tone,' p. 143.

independent of the manner in which the tones are produced, we are forced to conclude that the difficulty lies in the ear itself. We have, then, a plain indication that the vibrating parts of the ear are not damped with sufficient force and rapidity to allow of successfully effecting such a rapid alternation of tones."

According to the experimental evidence of the fatigue curves, the blurring or merging together of tones in the bass is not due to the peculiar construction of the ear, nor to insufficient damping of the resonance mechanism, but is the natural consequence of the fact that the tones of the scale are not separated by absolute numbers of vibrations, but by numbers determined by fixed ratios.

The difference in vibration frequency between two successive tones in the treble is very large when compared with the difference between two such tones in the bass; for example, the difference between c'' , 512, and d'' , 576, is 64 vibrations, whereas the difference between C_1 , 32, and D_1 , 36, is only 4 vibrations. In a run in the treble, therefore, each tone is so far moved from the one preceding that the arches stimulated by the first tone are altogether outside the region of influence of the second. It can very clearly be seen therefore that, when c'' , d'' , e'' , f'' , etc. are sounded in rapid succession, the effect will be distinct and brilliant. And the higher the pitch of notes with which the runs and trills are made, the more distinct will each tone be from the other, and the more brilliant the total impression.

In the bass, on the other hand, the opposite will be the case. The difference between two successive tones is comparatively very small. As previously noted, the difference between C_1 and D_1 is only 4 vibrations, while an octave higher it is only 8 vibrations. Since the difference in frequency between consecutive tones is so small, many of the arches responding to one tone will also respond to the other; in fact, nearly the same range will be influenced by each tone. The arches most strongly affected will be the resonals of each tone, and these are themselves not far distant from each other. In fig. 1, in which fatigue curves for five frequencies at the same pressure are shown, it will be noticed that the elevations for 152 and 163 overlap to some extent. The difference in frequency in this instance is eleven vibrations. If the difference in frequency were smaller, the overlapping would be greater; therefore the farther down in the bass one attempts to produce a rapid succession or alternation of tones, the more nearly will the same range of resonators be influenced by adjacent tones, and the more indistinct and

blurred will be the general impression. If semitones are employed instead of tones, the indistinctness will be proportionately increased.

The results of this investigation seem to find their natural explanation in terms of the resonance theory of audition, and therefore no present attempt has been made to interpret them in accordance with the Wrightson displacement theory.

This research was conducted under the auspices of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, to which body we wish to express our thanks.

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XII. *On the Effect of Fatiguing the Ear with Combinations of Two or more Tones.* By MOLLIE WEINBERG, M.A., M.Sc., University of Manitoba, Winnipeg, Research Student in Physics of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa*.

IN this communication, the method of studying the effects of aural fatigue by the critical frequency of pulsation or flutter of tones is applied to fatigue with two and three tones simultaneously.

The experimental arrangements were the same as described in previous communications †, except in one particular. In the former work, the source of continuous sound—a Stern Tonvariator—was enclosed in a large wooden box lined with thick felt. The box, however, transmitted some of the sound, so that the rotating disk did not completely produce the ideal alternations of sound and silence. In these experiments the upper part of the tonvariator was enclosed in a box made of pressed fibre, which is an extremely poor transmitter of sound. Watson ‡ found that a plate of this material, one-quarter of an inch in thickness, was capable of transmitting only one-tenth of one per cent. of the sound. Accordingly, a box of suitable size and shape was constructed of the fibre,

* Communicated by Prof. F. Allen, M.A., Ph.D. Read at the meeting of the Royal Society of Canada, Ottawa, May 1923.

† "On the Critical Frequency of Pulsation of Tones," *supra*, p. 50.

‡ Physical Review, vol. vii. p. 125 (1916).

in one side of which a circular hole was cut, through which the continuous stream of sound issued. Periodical interruption of the sound-ray was effected by a rotating disk in which were four symmetrically placed holes similar to that in the box. This arrangement gave sharp and clear flutterings of the tone, and, in consequence, the speed of the disk could be accurately and rapidly adjusted to the critical frequency of flutter, so that the pulsations of sound appeared just continuous. Unfortunately, the dimensions of the box interfered to some extent with the range of frequencies that could be studied, and consequently only part of one octave of tones could be employed. For the investigations described in this communication, however, it served the purpose extremely well.

I. *Application of the Critical Frequency of Pulsation of Tones to Tone Analysis.*

In a former paper* it was found that, when the ear was fatigued by exposure to any tone, the duration of the tone at the critical frequency of flutter or pulsation was increased over a range of about eight vibrations on each side of the frequency of the fatiguing tone. When similar measurements were made with the ear in its normal unfatigued condition, and the two plotted together, the fatigue curve appeared as a sharp elevation upon the normal, the peak of the elevation occurring at the frequency of the fatiguing tone.

In the experiments herein described, two or three additional tonvariators were used to give simultaneous fatigue with two or three tones of determined frequencies. Suitable calibrations of these instruments were made so that the exact frequencies were determined.

The arrangement of apparatus is shown in fig. 1, in which A indicates the air current, G the pressure gauge, T the tonvariator, D the disk, E the ear, and S the speed counter.

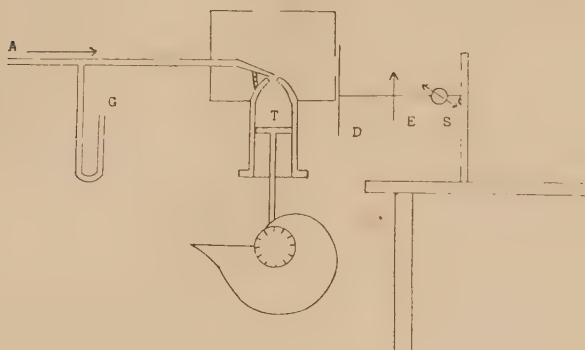
The method of procedure was as follows:—

At a definite blowing-pressure the tonvariator upon which measurements were to be made was adjusted to give a tone of definite pitch. The tonvariators used for the purpose of fatigue were then accurately tuned with it by eliminating beats, after which they were adjusted to give tones of desired frequencies. The left ear was then fatigued with these tones for two minutes by holding it close to the orifices of the

* "On the Effects of Aural Fatigue upon the Critical Frequency of Pulsation of Tones," *supra*, p. 126.

tonvariators. Immediately afterwards the measurement of the critical frequency of pulsation, or flutter, of a tone within the fatigued range of frequencies was made. The fatiguing process was again and again repeated, and similar measurements made at close intervals, over a range of frequencies including, and wider than, the range defined by the outermost fatiguing tones.

Fig. 1.



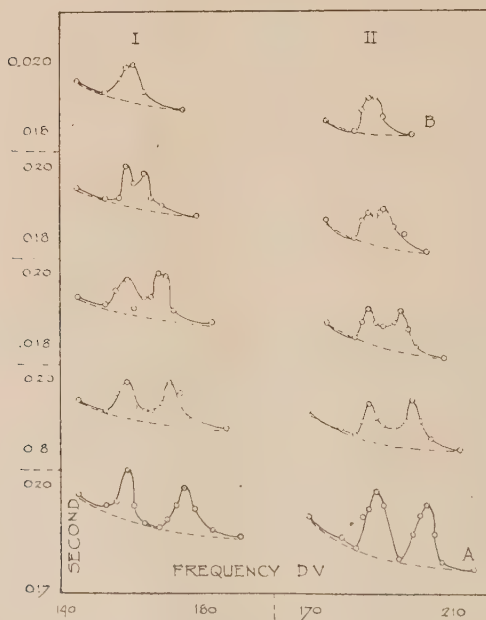
The first measurements were made with two fatiguing tones. These are tabulated in Table I., and the curves defined by them are shown in fig. 2.

The curve through the points not included in the elevation was taken to define the normal upon which the elevation is superimposed. This is indicated by the broken line. The elevation itself is similar to those obtained by fatiguing the ear with a single tone. The range affected by fatiguing, as shown by the width of the base of the elevation, is also approximately the same. In curve A the fatiguing tones were fifteen vibrations apart. Similar curves were obtained with fatiguing tones the frequencies of which, as shown in the table of values, slowly approached each other. Series I. in fig. 2 is such a set of curves. In this series the highest curve, B, was obtained with fatiguing tones that differed by two vibrations only, and curve A with tones that differed by fifteen vibrations; the intermediate curves were obtained with fatiguing tones which varied between these limits.

As can be seen from curve A, fig. 2, when the fatiguing tones are fifteen vibrations apart, there was very little overlapping in the elevations. Had they been about twenty vibrations apart, it is quite certain that each elevation would

be complete and distinct from the other, one elevation beginning at the point in the normal where the other ended. Interpreted according to the resonance theory of audition, this would seem to indicate that each of the fatiguing tones would affect a different set of arches—or whatever part of the resonating mechanism responds,—which, however, were adjacent to each other. From this it may be assumed that were the differences in frequency of the fatiguing tones greater than those used for these curves, the nature of the elevations would be the same, but with an increased extent

Fig. 2.



of normal curve between them—*i. e.*, the sets of arches influenced by the simultaneously fatiguing tones would be no longer adjacent, but would have a stretch of uninfluenced arches between them.

It can be seen from fig. 2, Series I., that, as the fatiguing tones approach each other, overlapping of the elevations takes place—*i. e.*, the curve between the maxima of the elevations no longer drops to the normal, but becomes more and more shallow until, when the difference in frequency is two vibrations, it has become a short, straight,

TABLE I.

Fatiguing with Two Tones simultaneously.

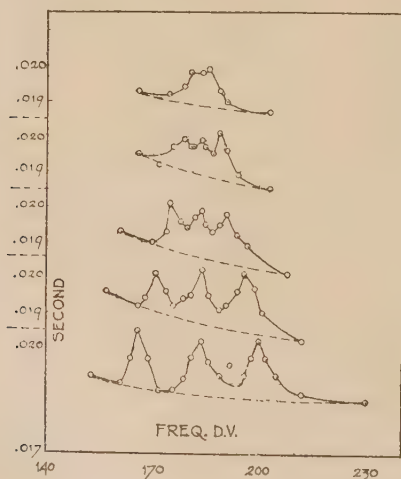
N.	D.	P.	N.	D.	P.	N.	D.	P.
I. Fatiguing Tones, 159 and 175.			I. Fatiguing Tones, 159 and 164.			II. Fatiguing Tones, 187 and 199 (<i>cont.</i>).		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
145	0·0198	1·60	145	0·0195	1·65	189	·0190	1·55
153	·0195	"	153	·0192	"	191	·0188	"
156	·0196	"	157	·0192	"	194	·0187	"
159	·0205	"	159	·0201	"	197	·0189	"
161	·0195	"	161	·0196	"	199	·0195	"
164	·0190	"	164	·0199	"	201	·0189	"
168	·0189	"	166	·0192	"	204	·0184	"
170	·0191	"	169	·0190	"	212	·0181	"
173	·0195	"	179	·0187	"	Fatiguing Tones, 187 and 196.		
175	·0200	"	Fatiguing Tones, 159 and 161.			D.V.	Sec.	Cm.
178	·0194	"	D.V.	Sec.	Cm.	175	0·0187	1·55
183	·0188	"	145	0·0195	1·65	183	·0183	"
191	·0186	"	153	·0192	"	185	·0187	"
Fatiguing Tones, 159 and 171.			157	·0196	"	187	·0191	"
D.V.	Sec.	Cm.	159	·0199	"	189	·0187	"
145	0·0195	1·60	161	·0200	"	191	·0186	"
153	·0192	"	164	·0192	"	194	·0187	"
156	·0197	"	175	·0187	"	196	·0190	"
159	·0200	"	II. Fatiguing Tones, 187 and 203.			198	·0185	"
161	·0193	"	D.V.	Sec.	Cm.	200	·0180	"
164	·0192	"	170	0·0192	1·55	208	·0177	"
166	·0192	"	179	·0186	"	Fatiguing Tones, 187 and 191.		
169	·0194	"	183	·0183	"	D.V.	Sec.	Cm.
171	·0200	"	185	·0192	"	175	0·0186	1·55
174	·0197	"	187	·0194	"	183	·0181	"
176	·0190	"	189	·0189	"	185	·0186	"
187	·0187	"	191	·0185	"	187	·0188	"
Fatiguing Tones, 159 and 168.			195	·0180	"	189	·0187	"
D.V.	Sec.	Cm.	199	·0187	"	190	·0188	"
145	0·0194	1·60	201	·0192	"	191	·0189	"
153	·0192	"	203	·0195	"	194	·0184	"
156	·0196	"	205	·0187	"	197	·0182	"
159	·0199	"	207	·0179	"	203	·0177	"
161	·0191	"	216	·0177	"	Fatiguing Tones, 187 and 189.		
164	·0194	"	Fatiguing Tones, 187 and 199.			D.V.	Sec.	Cm.
166	·0194	"	D.V.	Sec.	Cm.	175	0·0184	1·55
168	·0201	"	170	0·0192	1·55	183	·0181	"
170	·0200	"	179	·0187	"	185	·0187	"
172	·0190	"	183	·0185	"	187	·0190	"
183	·0187	"	185	·0189	"	189	·0190	"
			187	·0194	"	191	·0185	"
						199	·0180	"

horizontal line. In other words, as the fatiguing tones approach each other, more and more of the arches responding to the one tone will simultaneously be under the influence of the other fatiguing tone until, when the fatiguing tones are very close together, approximately the same range is influenced by each.

Fig. 2, Series II., is a set of curves obtained in a similar manner to Series I., which shows the same effects over a range of frequencies higher up in the octave. It serves, therefore, as a confirming experiment. The data are also given in Table I., in which N is the frequency, D the duration of the tone at the critical frequency of flutter, and P is the pressure to which the intensity is proportional.

The above sets of curves seem explainable by no other than a resonance theory. The evidence afforded by them may therefore be taken as strongly supporting the theory, that

Fig. 3.



some resonating mechanism by means of which complex tones may be analysed into their components exists in the ear.

A series of experiments similar to those above described was then carried out, in which three simultaneously fatiguing tones were used. This series of curves is shown in fig. 3, and was plotted from data in Table II. The three-elevation curves exhibit the same peculiar characteristics as do the previously described two-elevation curves. Here, again, when the fatiguing tones are about sixteen vibrations apart,

TABLE II.

Fatiguing with Three Tones simultaneously.

Fatiguing Tones, 166, 184, and 200.

N.	D.	P.
D.V.	Sec.	Cm.
153	0·0192	1·60
161	·0190	"
164	·0197	"
166	·0205	"
169	·0197	"
172	·0188	"
176	·0188	"
179	·0191	"
181	·0197	"
184	·0202	"
186	·0196	"
189	·0192	"
192	·0195	"
196	·0192	"
198	·0197	"
200	·0202	"
203	·0197	"
205	·0192	"
212	·0187	"
230	·0185	"

Fatiguing Tones, 171, 184, and 196.

N.	D.	P.
D.V.	Sec.	Cm.
157	0·0196	1·57
166	·0192	"
168	·0184	"
171	·0201	"
174	·0196	"
176	·0192	"
179	·0194	"
181	·0195	"
184	·0202	"
186	·0195	"
189	·0191	"
191	·0192	"
194	·0196	"
196	·0201	"
199	·0197	"
201	·0190	"
212	·0182	"

Fatiguing Tones, 175, 184, and 191.

N.	D.	P.
D.V.	Sec.	Cm.
161	0·0193	1·50
170	·0190	"
173	·0194	"
175	·0201	"
178	·0196	"
180	·0194	"
182	·0197	"
184	·0199	"
185	·0195	"
187	·0193	"
189	·0195	"
191	·0198	"
194	·0192	"
197	·0189	"
208	·0181	"

Fatiguing Tones, 179, 184, and 189.

N.	D.	P.
D.V.	Sec.	Cm.
166	0·0195	1·51
172	·0192	"
176	·0197	"
179	·0199	"
181	·0197	"
182	·0197	"
184	·0199	"
185	·0197	"
187	·0195	"
189	·0201	"
191	·0196	"
194	·0189	"
203	·0185	"

Fatiguing Tones, 181, 184, and 186.

N.	D.	P.
D.V.	Sec.	Cm.
166	0·0193	1·50
175	·0192	"
179	·0194	"
181	·0198	"
184	·0198	"
186	·0199	"
189	·0193	"
191	·0190	"
203	·0187	"

each elevation slopes down almost, if not quite, to the normal. As the differences between the frequencies of the fatiguing tones are decreased, the curves between the peaks of the elevations again recede from the normal until, when they have approached each other very closely, there is a short, straight, horizontal line between them. At that point approximately the same range of arches is influenced by each

fatiguing tone, and the resonals of each—*i. e.*, those arches possessing natural vibration frequencies corresponding exactly with those of the entering tones—are adjacent to each other. In all cases, whether fatiguing with two or with three tones, the maxima of the elevations define the resonals.

The curves indicating the effects of fatigue caused by three tones are thus seen to be exactly similar in character to those for two tones. It may therefore be justifiably assumed that were the ear to be fatigued with more than three tones simultaneously, by a method of procedure similar to the one above described, a set of curves would be obtained possessing peculiarities similar to those possessed by the curves in figures 2 and 3; in all cases the highest peaks of the elevations would define the resonals—*i. e.*, the resonating arches corresponding to the frequencies of the fatiguing tones.

The above therefore indicates an altogether new and very interesting method of tone analysis. To analyse a compound tone would only necessitate repeated fatiguing with the given mixture of tones, each fatiguing process being accompanied by a corresponding persistency measurement; the entire procedure being extended over a range of frequencies within which, it is judged, the component tones lie.

II. *An Experimental Study of Differential Tones.*

Combinational tones are heard when two musical tones of different pitches are sounded together loudly and continuously. They are of two kinds—differential and summational tones. The pitch number of the differential is equal to the difference of the frequencies of the generating tones; and that of the summational tone is equal to the sum of the frequencies of the generating tones.

There are different orders of combinational tones. The differential, or combinational tone of the first order, is one of pitch equal to the difference of the vibration frequencies of the generating tones themselves. Combinational tones of the second order are formed by the combination of the generating tones with differentials of the first order. These again produce new combinational tones with other differentials. There are thus differential tones of many orders, the first-order differential being the loudest, the intensity decreasing rapidly as the order of the differential becomes higher.

This investigation deals with differential tones of the first order only.

The successful results obtained in investigating the effects of aural fatigue suggested the application of that method to determine the probable nature of the combinational tone.

The apparatus used was the same as that employed in the investigation in the first section of this paper.

The method of procedure was as follows:—

Two tonvariators were adjusted to give tones of such frequencies that their differential of the first order fell somewhere within the range of frequencies upon which measurements of the critical frequency of pulsation could be made. The true frequency of the differential tone was obtained from the calibration curves of the tonvariators made by comparison with tuning-forks. Fatiguing with the two generating tones simultaneously, and proceeding in a manner similar to that described in the previous section, measurements of the critical frequency of pulsation were made at very short intervals over a sufficiently wide range of frequencies which included the differential tone of the first order.

The resulting curves, plotted from the data in Table III.,

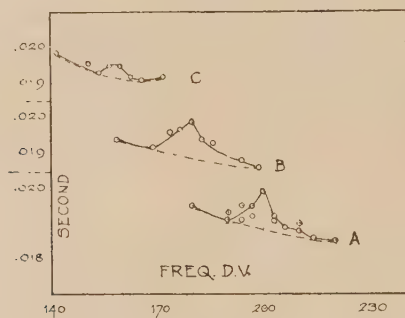
TABLE III.

Differential Tones of the First Order.

N.	D.	P.	N.	D.	P.
A. Generating Tones, 170 and 370.			B. Generating Tones, 220 and 400.		
Differential Tone, 200.			Differential Tone, 180.		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
180	0·0195	1·55	159	0·0194	1·50
190	·0191	„	169	·0192	„
194	·0195	„	174	·0196	„
197	·0195	„	177	·0197	„
200	·0199	„	180	·0199	„
203	·0191	„	183	·0194	„
206	·0189	„	186	·0193	„
210	·0190	„	194	·0188	„
214	·0186	„	199	·0186	„
220	·0185	„			
C. Generating Tones, 150 and 350.			C. Generating Tones, 220 and 380.		
Differential Tone, 200.			Differential Tone, 160.		
D.V.	Sec.	Cm.	D.V.	Sec.	Cm.
180	0·0195	1·55	142	0·0199	1·45
190	·0193	„	151	·0196	„
194	·0191	„	154	·0193	„
197	·0192	„	157	·0195	„
200	·0199	„	160	·0195	„
203	·0192	„	163	·0192	„
206	·0189	„	166	·0191	„
210	·0188	„	172	·0192	„
220	·0185	„	182	·0191	„

are given in fig. 4. Each graph is seen to be a portion of a normal curve, broken by a short elevation similar to that obtained by direct fatigue. The peak of the elevation is at a frequency which very closely approximates that of the differential. Curve A is the average curve drawn through two sets of measurements, both for the differential tone of frequency 200, the generating tones of each set differing by that number. The frequencies of the generating tones are given in the table. This indicates that no matter what the generating tones may be, the combinational tone will influence the same portion of the resonating system if the difference of their vibration frequencies is the same.

Fig. 4.



Curves B and C were obtained in a similar manner to A, but for differing pitches of the differential. The characteristics of all the curves appear to be the same. Curve C is a little shallower than A and B.

The position of the maximum height of the elevations represents approximately the pitch of the differentials. The vertical heights of these elevations, however, are not as great as those representing fatigue caused by ordinary tones. This difference is probably due to the comparatively low intensity of the differential tones.

The graphs discussed may, with the aid of the resonance theory of audition, be interpreted in such a manner as to explain the probable nature of the differential tone. The elevations indicate that the differentials have as direct an effect upon portions of the series of resonating arches as have tones generated in the ordinary manner—*i. e.*, differential tones are objective in character.

It was formerly believed that combinational tones were subjective effects—*i. e.*, purely psychological phenomena.

Helmholtz * himself stated that there were both objective and subjective combinational tones. Preyer † carried out a series of experiments which seemed to prove the subjectivity of differential tones. The experimental evidence as given above, however, supports the theory that differential tones of the first order are objective, since they possess the same peculiarities of stimulation as do tones produced in the ordinary manner. In other words, they are physiological and not psychological in their origin.

It was hoped to carry through a series of experiments similar to those above described for summational tones. Since this would necessitate the taking of measurements over a range of frequencies far higher than that which could be measured with the experimental arrangements at the time, their study had to be postponed until the apparatus could be improved to allow measurements to be taken over a more extended range of frequencies.

Many attempts were therefore made to adapt the apparatus to higher octaves. But with frequencies above 300 d.v. the rotating disk was incapable of giving sufficiently marked alternations of intensity of the sound to be of any value. A new method of interruption of the sound-ray was found, but it has not yet been sufficiently developed to give reliable measurements.

In conclusion, it may be stated that the results of this investigation support the theory formulated by Helmholtz, that tones are perceived and differentiated from each other by means of a resonance mechanism which exists in the internal ear. From this general statement it is also clear that differential tones and probably summational tones are not excluded.

I wish to acknowledge my indebtedness to the kindness and valuable advice of Dr. Frank Allen, Director of the Department of Physics of the University of Manitoba, at whose suggestion and under whose direction the investigations here described were carried out.

I also desire to express my thanks to the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, under whose auspices this investigation was conducted.

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Winnipeg, Manitoba.

* Helmholtz, 'Sensations of Tone,' p. 531.

† *Loc. cit.* p. 531.

XIII. *On a Supposed Limitation of the Second Law of Thermodynamics.* By ENOS E. WITMER, Ph.D., *Harrison Research Fellow at the University of Pennsylvania* *.

IN an article in the *Phil. Mag.* (6) vol. xliii. p. 1047 (1922) Fairbourne gives a proof that if a vessel of suitable shape, typically a truncated cone open at both ends, be immersed in a gas so rarefied that the mean free path of the molecules is large compared with the dimensions of the vessel, the molecules entering in haphazard directions will be diverted to leave in one preponderating direction. This state of affairs would be contrary to the second law of thermodynamics, assuming its applicability in this case, since a paddle-wheel properly placed with respect to the vessel would yield mechanical work at the expense of the thermal energy of the gas. To many physicists the conclusion suggested that the argument was fallacious. The fallacy exists, and is pointed out below, I believe, for the first time.

Fairbourne's proof, for the details of which reference must be made to the original article, is based upon the following assumptions, expressed or implied:—

1. That the mean free path of the molecules of the gas surrounding the vessel is so great that intermolecular collisions in the vessel are occurring with only a negligibly small fraction of the total number of molecules which pass through in a representative period of time.

2. That regular reflexion of the molecules takes place at the sides of the vessel.

3. That there are no forces of attraction or repulsion between the sides of the vessel and the gas molecules.

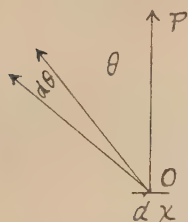
4. In the course of the argument, which is carried out in two dimensions, he explicitly makes the apparently justifiable assumption that at any point O in the face of the vessel "molecules will enter equally in all directions throughout 180° ."

The first three assumptions are admissible; the last one properly interpreted is also, but as it is applied in Fairbourne's proof, and as one would naturally interpret it, it is not admissible. The term "point" in this assumption is misleading. As is frequently the case in physics, the word "point" is used in Fairbourne's proof to signify not a point, strictly speaking, but an element of length. Put into rigorous terms, the last assumption, naturally interpreted, is that

* Communicated by Professor Bazzoni.

through the elementary length dx at the point O, molecules will enter equally in all directions throughout 180° . This statement is manifestly untrue.

Fig. 1.



Let dx be an element of length, OP the normal directed toward one side, and θ the angle between any direction and OP. Then if dn is the number of molecules crossing dx in directions included between θ and $\theta + d\theta$ in a time dt ,

$$dn = N \cos \theta \, dx \, d\theta \, dt, \quad \dots (1)$$

where N is a constant.

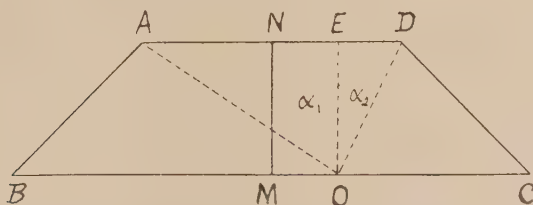
The false assumption discussed in the last paragraph is equivalent to the omission of the factor $\cos \theta$ in (1).

The number of molecules dn_1 which cross dx in directions included between $\theta=0$ and $\theta=\alpha$ is

$$\begin{aligned} dn_1 &= N \, dx \, dt \int_0^\alpha \cos \theta \, d\theta \\ &= N \sin \alpha \, dx \, dt, \quad \dots (2) \end{aligned}$$

We shall now carry through the reasoning with the modification indicated for the first vessel considered by Fairbourn, and show that the same number of molecules pass through the vessel upwards as downwards.

Fig. 2.



The two-dimensional vessel is ABCD (fig. 2). AB and CD are the sides, while AD and BC are open.

$$\angle ABC = \angle BCD = 45^\circ,$$

AD is parallel to BC,

$$AN = ND = MN = a,$$

and $BM = MC = AD = 2a.$

Let $MO = NE = x.$

We shall first derive an expression for the number of molecules which enter through BC and pass out through AD. There are two cases to consider.

(a) For points under AD.

For such points $-a < x < a$.

It can easily be shown that in this case only molecules whose directions are included in $\angle AOD$ pass out through AD from the element dx at O, the rest being reflected through BC.

$$\begin{aligned}\text{But} \quad \angle AOD &= \angle AOE + \angle DOE \\ &= \alpha_1 + \alpha_2.\end{aligned}$$

And from (2) the number of molecules passing through the element dx (determined by x and $x + dx$) and out through AD is

$$n_2 dx = N(\sin \alpha_1 + \sin \alpha_2) dx dt.$$

For $x > 0$,

$$n_2 dx = N \frac{(a+x) dx dt}{\sqrt{a^2 + (a+x)^2}} + N \frac{(a-x) dx dt}{\sqrt{a^2 + (a-x)^2}}.$$

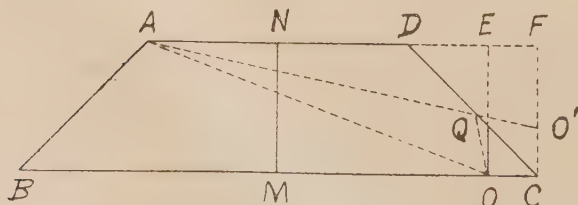
Integrating, the number of molecules passing out through AD from points under AD is

$$\begin{aligned}\int_{-a}^a n_2 dx &= 2 \int_0^a n_2 dx \\ &= 2Ndt \left[\sqrt{a^2 + (a+x)^2} - \sqrt{a^2 + (a-x)^2} \right]_0^a \\ &= 2Na(\sqrt{5} - 1)dt. \quad \dots \dots \dots (3)\end{aligned}$$

(b). For points under the sides

AB and CD, i. e. $|x| > a$.

Fig. 3.



In fig. 3 let O' be the reflexion of O in CD , and Q the intersection of CD and $O'A$. Then $\angle AQD = \angle CQO$.

It is easily seen that only molecules whose directions are included in $\angle QOA$ pass out through AD from O.

Since $\angle BCD = 45^\circ$,

$\angle O'CO = 90^\circ$,

and $DF = a$.

Let OE be normal to BC.

Then $\angle QOA = \angle AOE - \angle QOE$.

But $\angle QOE = \angle O'AF$;

hence $\angle QOA = \angle AOE - \angle O'AF$.

$$\equiv \alpha_1 - \alpha_2.$$

Hence in this case

$$n_2 dx = N(\sin \alpha_1 - \sin \alpha_2) dx dt;$$

and for $x > a$,

$$n_2 dx = N \frac{(x+a) dx dt}{\sqrt{a^2 + (x+a)^2}} - N \frac{(x-a) dx dt}{\sqrt{9a^2 + (x-a)^2}}.$$

Integrating, the number of molecules passing out through AD from points for which $|x| > a$, i. e.

$$\begin{aligned} 2 \int_a^{2a} n_2 dx &= 2N dt \left[\sqrt{a^2 + (x+a)^2} - \sqrt{9a^2 + (x-a)^2} \right]_a^{2a} \\ &= 2Na dt (3 - \sqrt{5}). \end{aligned} \quad (4)$$

Hence, adding (3) and (4), the number of molecules passing upward through AD is $4Na dt$.

From (2) the number of molecules passing from one side to the other is

$$2N dx dt \sin \frac{\pi}{2} = 2N dx dt.$$

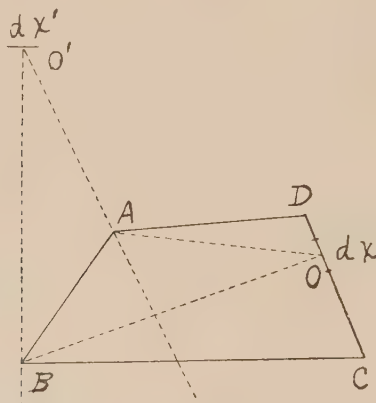
Hence the number of molecules passing downward through AD is also $4Na dt$.

This shows that the same number of molecules pass upward through a vessel of the specified shape as downward.

We shall now give a proof that applies to any two-dimensional vessel ABCD where AB and CD are sides of the vessel, AD and BC being open. This will include both the vessels studied in detail by Fairbourn. Here it is necessary to consider the directional distribution of the molecules at a point. We shall say that the directional distribution of the impinging molecules is normal at a point P and within the $\angle APB$ if eq. (1) applies to an element of length dx placed at P for all molecules which impinge in directions included in

$\angle APB$, and if further the N that applies is the N for a point within the mass of the gas—*i. e.*, a point at least three or four mean free paths from the boundary of the gas. The normal directional distribution of the molecules reflected from a point on a surface is defined in a similar manner. We shall further assume that for a point on or near the boundary the directional distribution of the impinging molecules is normal at that point and within a given angle, unless there is a boundary of the gas in that angle within a radius of three or four mean free paths.

Fig. 4.



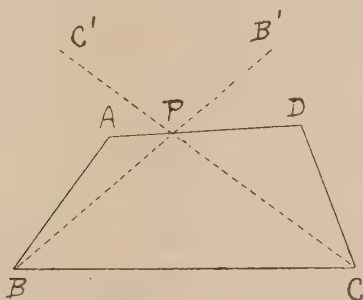
Of the molecules entering ABCD, some collide with the sides, some pass through without collision, but only a negligibly small number collide with other molecules.

Let us consider first those that impinge on the sides AB and CD in fig. 4. We wish to determine the number of molecules that enter through AD and collide with the sides as compared with the number that pass out through AD after reflexion from the sides; likewise for BC. In doing this we must be careful to count every molecule, and not to count any molecule more than once. It is evident that every molecule that impinges on a side will impinge for a first time after entering the vessel, and for a last time before leaving the vessel. Therefore, if at any given point of the sides we count only the molecules which enter directly or leave directly, we shall count all, and not count any more than once.

In fig. 4 consider an element dx at the point O on the side CD. Of the molecules leaving dx , all ultimately get out

through AD and BC, some directly, some only after a number of reflexions. For the sake of simplicity, suppose that all escape after no more than one reflexion, and that all the reflected molecules get out through BC. Since every path is reversible, this argument shows that molecules will strike dx in all possible directions. We shall now show that the directional distribution of the molecules impinging on dx is normal. Since $\angle AOB$ and $\angle COB$ face the free gas, it is easily seen that in these angles the directional distribution of the impinging molecules is normal. To determine the directional distribution at O in $\angle AOB$, consider dx' the reflexion of dx in AB. Since any path in $\angle AO'B$ which would lead to dx' at a given inclination to its normal if AB were not present leads to dx at the same inclination to its normal, it is easily seen that the directional distribution in $\angle AOB$ at O is the same as it would be in $\angle AO'B$ at dx' if AB

Fig. 5.



were removed. But the latter directional distribution would be normal since the angle faces free "space." Hence the directional distribution of the molecules impinging at O is normal in the entire $\angle DOC$. But regular reflexion on a plane leaves a normal distribution normal. Hence the same number of molecules return from dx through AD as entered through AD and impinged on dx . Since this is true for every elementary length on AB and CD, it follows that of the molecules impinging on the sides the same number go out through AD as entered through AD; likewise for BC.

Of the molecules that pass through but do not collide with the sides, all pass through AD. Consider an elementary length dx at P on AD in fig. 5. Only molecules whose directions of motion lie in $\angle BPC$ or $\angle B'PC'$ pass through without collision with the sides. Since these angles facing free "space" are equal and similarly situated with respect to dx , it follows that the same number of molecules leave through

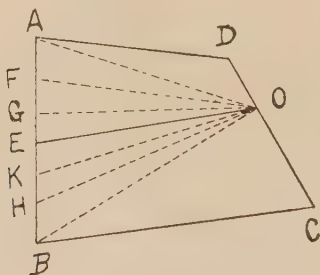
AD without collision with the sides as enter through AD and do not collide with the sides.

It follows, then, that the same number of molecules leave through AD as entered through AD, and likewise for BC.

It is easily seen that, by taking into consideration the velocities of the molecules, the argument above will show that the pressure at every point on AB and CD is the same as the pressure at any point within the mass of the gas—*i. e.*, at a point more than three or four mean free paths from the boundary. In other words, the pressure is normal at all points on the sides of the vessel.

It is evident that the same process of reasoning can be applied in the case where some molecules escape from the vessel only after a number of reflexions. Consider first the molecules that collide with the sides. Thus, if fig. 6 represents the general case, we can say that of the molecules leaving the element dx at O some ultimately go out through

Fig. 6.



AD, the remainder through BC. Furthermore, we can divide up the straight angle DOC into angles AOD , FOA , COB , etc., such that all the molecules leaving the element dx at O in directions included in any one of these angles will suffer the same number of reflexions, and ultimately go out through the same open face. To be definite, let us say that all the molecules leaving O in directions included in $\angle DOE$ escape through AD, those in $\angle AOD$ directly, those in $\angle FOA$ after one reflexion, those in $\angle FOG$ after two reflexions, etc., while below in like manner all the molecules leaving O in directions included in $\angle COE$ go out through BC, those in $\angle BOC$ directly, those in $\angle HOB$ after one reflexion, etc. Since every path is reversible, all molecules impinging on the element dx at O within any one of these angles will have undergone the same number of reflexions, and have entered through the same open face. Now, just as in the case of one

reflexion we showed that the directional distribution of the molecules impinging at O was normal, so it can easily be shown that for any number of reflexions the directional distribution of the impinging molecules will be normal at O. Having shown this, the rest of the argument follows as before.

It is easily seen that the same sort of argument applied to any point within the vessel ABCD will show that the gas-pressure and directional distribution of the molecules is also normal at that point.

So far, the argument has been confined to two dimensions. It is easily seen, however, that the process of reasoning, using the method of reflexion applied in the last two cases, could be applied to a three-dimensional vessel of the shape of a truncated pyramid, the upper and lower bases being open. It could, therefore, be applied to a vessel of the shape of a truncated cone, since the latter could be regarded as the limiting case of a truncated pyramid of many sides.

We have demonstrated, therefore, that for the type of vessels considered in this paper there is no movement of the gases in one preponderating direction. Furthermore, the type of reasoning applied above to the vessel in fig. 6 could be applied to vessels of various shapes; and it is highly probable, therefore, that there is no shape of vessel that will produce a movement of the gas in one preponderating direction.

The author acknowledges his indebtedness to Professor C. B. Bazzoni, who suggested this investigation.

XIV. *Ultimate Rational Units.*

By NORMAN CAMPBELL, *Sc.D.**

SUMMARY.—The paper contains a criticism of Prof. Lewis's theory of "ultimate rational units." It is argued that the theory is demonstrably false, and arises merely from a failure to observe that the equations by which Planck proposes to determine his "natural units" from universal constants are usually indeterminate.

After the proof is completed a few general observations are offered on the assumptions and arguments on which the theory is based

1. **T**HE theory of ultimate rational units was propounded by Prof. G. N. Lewis † in the *Phys. Rev.* iii. p. 92 (1914); extended in *J. Amer. Chem. Soc.* 44, p. 1008 (1922);

* Communicated by the Author.

† Since in the last paper Prof. Lewis takes entire responsibility for the theory, I have omitted all reference to those with whom he was associated in the earlier publications.

and re-stated in *Phil. Mag.* xlv. p. 266 (1923). These papers will be denoted as (I), (II), (III). I propose to criticize this theory; and at the outset would offer some apology for occupying valuable space with purely destructive arguments which are, moreover, belated.

My apology is that the need for criticism has only arisen recently. It has always appeared to me that the arguments on which the theory is based are utterly unsound; but for many years, since nobody seemed to take the theory seriously, I imagined that others shared my opinion. But it now appears that the very simple fallacy on which the theory is based is not generally understood. Mr. Dushman* has recently taken the theory quite seriously in interpreting some valuable experiments; Prof. Lewis has challenged criticism by re-stating his theory in a very positive manner in (III); and—most significant of all—"O. J. L.," in appending to this last paper some general objections to Prof. Lewis's arguments (in which I concur entirely), has omitted to draw attention to the simple reasoning whereby it can be demonstrated to be false.

One further word of explanation. The theory of U.R.U. (if I may use the abbreviation) is concerned with units and dimensions. In my 'Physics' I ventured on some criticism of the current exposition of this subject. It is important, therefore, to insist that the arguments I am about to advance have nothing whatever to do with any new or unorthodox views. They are all implied by the well-known reasoning on which Planck based his "natural units"; in fact, I should gather from Planck's exposition of that subject that he judged the errors which have led Prof. Lewis astray too obvious to be worth noticing explicitly. It is only when, by the most strictly orthodox reasoning, I have disposed of U.R.U., that I shall offer a few general remarks which may be (though they should not be) slightly less familiar.

2. The theory of U.R.U. is stated thus by its author:—(III, p. 270) "There is possible a set of units in terms of which all universal constants (and not merely those which are employed in defining the units) will be reduced to simple numbers." I admit at once that the theory, expressed in this form, is not demonstrably false; indeed, at some time in the future it may appear obviously true (see p. 172 below). But that is only because there is ambiguity in the terms "all universal constants" and "simple numbers." The first ambiguity

* S. Dushman, *Phys. Rev.* xxi. p. 623 (1923).

we shall find not directly important for our purpose ; but we must have some clear idea of what numbers are simple. We can gather enough indication from Prof. Lewis's use of his theory. He deduces from it the proposition that, if a set of units are chosen so that some universal constants are represented by certain simple numbers, then there is a presumption that any other universal constant is to be represented in terms of these units by a simple number, and that therefore evidence can be produced for a universal constant having one value rather than another. This last conclusion does not follow unless it is asserted of simple numbers (1) that not all numbers are simple, (2) that the simplicity of a number is something that can be determined before it is known whether it is actually the value of a universal constant. If these propositions are admitted, we know enough about simple numbers to proceed with our proof.

3. Let us proceed to discuss generally how a set of units may be chosen to give universal constants assigned values. We shall assume nothing more than the elementary principles of the most orthodox theory of dimensions, according to which there are certain fundamental magnitudes, f in number, the units of which may be fixed independently of each other, while all other magnitudes (including the n universal constants) have dimensions in terms of these magnitudes. What precisely is meant by the latter part of this assertion is best described by the equations (1) which we are about to state.

Let U_1, \dots, U_f be the fundamental magnitudes, A_1, \dots, A_n the universal constants. Let a_1, \dots, a_n be the numerical values of these constants in terms of the fundamental units by means of which they have actually been measured ; this set of units will be termed "practical units." (*E.g.* if A_1 is the velocity of light, and c.g.s. units are practical units, $a_1 = 3 \times 10^{10}$.) Let a'_1, \dots, a'_n be the numerical values which it is proposed to assign to the universal constants in the hope of finding some set of units which will give these values. If such a set can be found, let u_1, \dots, u_f be the numerical values of these fundamental units in terms of the practical units. Further, let d_{rs} be the dimensions of A_r in terms of U_s . Then, in virtue of the principles assumed, there must be a relation between the numerical values and the

The condition is that there shall be some solution of equations (2), *i. e.* some set p_1, q_1, \dots, s which satisfy them. The result important for our purpose is that if $n=f+n'$, where n' is positive, there are at least n' solutions, no one of which can be deduced from the others. If n' is negative or zero, there may or may not be a solution. This result would fail only if equations (2) were not independent, and if there were some necessary relations between p_1, q_1, \dots, s ; that is to say, only if there were some dimensions which a universal constant could not have. So far as I am aware, neither Prof. Lewis nor anyone else has suggested a possible limitation on the dimensions of universal constants; the matter need therefore not be discussed. But it may be well to remark that, if there is a limitation, it is still possible to prove that U.R.U. is false in all the applications which have been so far made of it.

If n' no-dimensional magnitudes (and not only 1) can be formed of the n constants, these being independent in the sense that none of the no-dimensional magnitudes can be formed by simple combination of the others, then there will be no solution of (1) unless n' equations of the form (3) are all true; and if they are true, then the number of equations (1) is effectively reduced to $n-n'$ *.

4. With these considerations as a guide, we can state exhaustively what conditions can occur when we try to determine a set of f units by assigning values to n constants, and whether, in each of them, the determination is possible.

I. It is impossible to form a no-dimensional magnitude from the n constants.

a. $n > f$. The case cannot occur.

b. $n = f$. A single set of units can be determined, whatever values are assigned to the constants.

c. $n < f$. Infinitely many sets of units will give the assigned values, whatever they may be.

II. It is possible to form n' no-dimensional magnitudes, but the values assigned to the constants are such that one or more of the resulting equations (3) are not true.

No set of units will give the assigned values.

* The purely algebraic argument may be found difficult by some readers. But they will speedily find out the significance of what has been said if they will try to determine a set of units of mass, length, time which will give assigned values (say unity) to the 3 constants, e, h, c , which form the no-dimensional combination $e^2 h^{-1} c^{-1}$.

III. It is possible to form n' no-dimensional magnitudes, and the values assigned are such that all the resulting equations (3) are true.

a. $n > f + n'$. The case cannot occur.

b. $n = f + n'$. A single set of units can be determined, whatever values are assigned to $n - n'$ of the constants, those assigned to the remaining n' being such as to make the n' equations (3) true.

c. $n < f + n'$. Infinitely many sets of units can be determined, whatever values are assigned to $n - n'$ of the constants.

For completeness a word should be added about experimental error. The numerical values a_1, \dots, a_n are, of course, never known exactly; equations (1) and (3) should be replaced strictly by inequalities assigning limits. The effect of such a substitution on the conclusions just stated would be to replace in I. b and III. b "a single set of units" by "a single set of ranges within which the units must lie." But conciseness and no inaccuracy follow from the neglect of this complication.

An examination of our conclusions shows that, in deciding what set of units, if any, will give assigned values to universal constants, it cannot possibly be relevant whether those values are simple. For if the conditions are such that a set can be determined uniquely at all, there are either no limits on the choice of assigned values (I. b) or the limits are imposed by equations, involving experimental values, which cannot be judged to be true or untrue before those values are known. There is no room anywhere for the conception of simple numbers, which are a special class recognizable before the experimental determination is complete. While therefore we have to admit (owing to the vagueness of the terms involved) that it is impossible to prove that U.R.U. is not true, we can assert that, if it is true, it is equally true when for "simple" we write "simple or not simple." Accordingly it cannot possibly afford any justification for any kind of presumption that any numerical value is likely to be simple rather than not simple.

5. With that proof my main task is accomplished. But before proceeding to more general matters, it may be well to classify according to the table just given the cases considered by Prof. Lewis. But before this can be done, some preliminary observations are necessary.

It is remarkable that the author of U.R.U. does not profess to have determined the set of units which make all universal constants simple numbers. The omission may seem significant; for it might be thought that, if the theory was true, it would be merely a question of a little arithmetical labour to give this, the most convincing, proof of it. But this criticism of Prof. Lewis's work would overlook the difficulty of deciding what numbers are simple according to his ideas. I have not been able to discover exactly what his views on this subject are; and, since they seem to lead to some surprising conclusions, it is fortunate that it is possible to prove U.R.U. to be false without coming to any very exact decision on the matter. But this difficulty (or possibly some other), which has prevented him from taking the obvious course, has led to a curious procedure. He has taken throughout the centimetre as the unit of length and assigned values to universal constants so as to determine the other fundamental units. Here again is a difficulty in the argument which again, fortunately, we are able to avoid; for it is by no means clear how many fundamental units (or magnitudes) Prof. Lewis thinks there are. His practice would seem to indicate that he takes the conventional view that there are 4, namely length (l), time (t), temperature (θ), and either mass (m) or energy. But his deliberate statements would seem sometimes to suggest that he thinks that we have some choice in the matter, and that we might, if we pleased, take only one fundamental magnitude. This doubt does not affect the proof that has been given; for that proof holds whatever value is assigned to f . But in order to classify his instances it is convenient, and will save much discussion, to come to some decision on the matter. I shall assume that there actually are four fundamental units; that choice will offer the greatest chance of making his arguments intelligible to the many others who take that view*.

If, then, there are 4 fundamental units and Prof. Lewis chooses arbitrarily the centimetre as one of them, he has three to determine. In his first application of U.R.U., in order to determine these three, he assigns values to 4 universal constants, namely c (velocity of light), k (Boltzmann constant), e (electronic charge), a (Stefan's constant).

* As it happens, I agree with Prof. Lewis in holding that the assertion that there are 4 fundamental units is an inadequate way of expressing the facts, although, if reasonable care is taken, it does not lead often to actual error. But while he wants to reduce the number of fundamental magnitudes, I want to increase it.

This last constant he defines, in a rather unusual manner, by the relation $E = a \cdot V\theta^4$, where E is the energy in volume V in the interior of a black body at temperature θ . One and only one combination of these constants is no-dimensional, namely $a\epsilon^6 k^{-4}$. Accordingly $f=3$, $n=4$, $n'=1$. His case can be made to fall under III. *b*, and he can define his three fundamental units unambiguously whatever values he assigns to his constants, so long as these values are consistent with the single condition $a\epsilon^6 k^{-4} = a'\epsilon'^6 k'^{-4}$. Within experimental error $a\epsilon^6 k^{-4} = (4\pi)^{-6}$; so the values he chooses, namely $c' = k' = a' = 1$, $\epsilon' = \frac{1}{4\pi}$, will suffice. But infinitely many other sets of values would serve equally well.

In his second application (II.) his constants are c , k , ϵ , C_1 . C_1 is a constant defined by an equation due to Sackur, relating to the entropy of a monatomic gas. It has the dimensions $m^{-3/2} l^{-3} \theta^{-3/2}$, and $C_1 = 3.3 \times 10^{-3}$ (about). Here again there is one and only one no-dimensional combination of the constants, namely $c^6 k^3 \epsilon^{-12} C_1^{-2}$. The case again can be made to fall under III. *b*. The values assigned to c' , k' , ϵ' are the same as before; the simple value he assigns to C_1' is $N^{-5/2}$, where N is the number of molecules in a gram-molecule*. Since within experimental error

$$c^6 k^3 \epsilon^{-12} C_1^{-2} = (6.2 \times 10^{23})^5 \times (4\pi)^{12},$$

the values will serve to determine the 3 units, but so also will infinitely many other sets of values.

If the two instances are combined, we have $n=5$, $f=3$. But no further independent no-dimensional combinations are introduced. ($c^6 k^{-5} a^2 C_1^{-2}$ and $c^{-24} a^{-3} \epsilon^{30} C^8$ are no-dimensional, but they result from combination of the two original no-dimensional magnitudes.) Accordingly $n' = 2$, and the retention of the same values assigned to the constants brings the instance again into III. *b*.

* Here I cannot refrain from inserting one numerical criticism, although, as I have explained, it has nothing to do with my main thesis. It is surely remarkable that the number of molecules in a gram-molecule should be a simple number in whatever units we choose to measure mass. Can Prof. Lewis and his associates in this part of his work have overlooked the fact that in assigning to C_1 the value $N^{-5/2}$, they are assigning a value which they must retain whatever unit of mass results from that assignment? It is only if the gram results as the unit of mass that the value of C' will be a simple power of the number of molecules in a quantity of the gas having M times unit mass, where M is the molecular weight. The arguments offered for the simplicity of this value are quite beyond my comprehension. But, once more, even if they are perfectly sound, that does not affect the falsity of U.R.U.

6. The fact that all instances fall in this class suggests how Prof. Lewis may have been led astray. In hazarding this guess, I am obviously taking a risk; and if Prof. Lewis denies that such was his train of thought, I have no defence to offer. But to indicate how the fallacy might have been reached may perhaps save others from the mistake. I suggest then that he started with a belief in U.R.U. He found that if the constants he chose for discussion (I cannot suggest why he originally chose so curious a constant as his a) were to determine any set of units at all, the values he assigned to them must satisfy equation (3). He found that he could assign simple values which would satisfy equation (3). He concluded, with perfect logic, that U.R.U. could not be true unless the constants had these simple values; in the technical sense, U.R.U. "implies" that the constants have these values. But he overlooked the well-known fact that a false proposition implies all propositions, true and false. He could not at the same time prove both that U.R.U. was true and that the constants had these values. Indeed, if he had not been obsessed by his belief in U.R.U., he would have observed that there were infinitely many sets of values assigned to his constants which would enable him to determine from them a set of units. This fact, if he had observed it, strongly suggests that U.R.U. is false; for U.R.U. suggests that the set ought to be unique. The argument therefore is not analogous to one with which he may have been inclined to compare it. If I invent a theory (say Planck's theory) which predicts that a numerical relation holds between universal constants (say $h^3 = \frac{8\pi^2 k^4}{15c^3 a}$), and if I find that the experimental measurements are consistent with this relation, then I am apt to conclude both that the theory is true and that the magnitudes are connected exactly by the relation. The argument—though I would not throw the slightest doubt on its validity—is logically inadmissible on account of the universal implication of false propositions. But there is a very essential difference between this argument and that which I am venturing to impute to Prof. Lewis—namely, that in the sound argument there is nothing, and, from the nature of the argument, can be nothing, in the conclusion which throws doubt on the premisses.

7. On this view Prof. Lewis's error arose from his presumption that U.R.U. was true. How came he to entertain at all a theory so easily demonstrated to be false? He seems to have told us; he apparently believes that by some juggling

with dimensions he can rid science of all "arbitrary" numbers. This belief is, of course, directly contrary to the views that most of us hold; but if it can be seriously entertained, it may not be a waste of time to inquire once more into the nature and source of the arbitrary element in all measurement.

Consider first fundamental* measurement, the process by which we assign numerals to represent properties (magnitudes) without making use of a similar process previously established for other properties. The possibility of measuring a magnitude fundamentally depends on the truth of certain laws. The form of these laws is such that, while it is necessary to measurement that we assign the numeral 1 to one of the systems having the magnitude, it is immaterial to which of the systems we assign that numeral; whichever system we select as a unit, we can still measure all of the remaining systems. That perfect liberty of choice is a consequence of the form of the laws; if the laws were other than they are, it is possible that we might have to adopt some other kind of measurement in which we should not have that liberty. But we have to take laws as they are. Prof. Lewis says that "there is nothing nature abhors more than an arbitrary number"; but (to retort in his own phraseology) it is nature herself who, by framing laws as she has framed them, forces this arbitrary choice upon us.

In one respect it may seem that the statements just made need modification. There are certain magnitudes (or it may be so admitted here) which, when we have measured them, turn out to be all integral multiples of a single unit. Now, if we only developed our system of measurement so far as to permit of the measurement of integral multiples of the unit, and if we made use only of the laws which permit this development, then there would truly be a limitation in the choice of unit. Unless we chose our unit in a certain way, we should not be able to measure all the systems having the magnitude; we should have no choice if we were to measure completely. But there is no reason why we should stop the development of measurement at this point; even when these magnitudes are concerned, the laws which permit fractional measurement are still true; and if we make use of these laws, as we do with other magnitudes, we have still complete freedom in the choice of unit. Even here, where, as Prof. Lewis would say, nature might reasonably have limited our choice, she still prefers to leave it unlimited.

* I am using the term fundamental here in the sense explained in 'Physics,' Ch. x.

It follows that the statement that any fundamental magnitude has any particular numerical value is arbitrary, in the sense (I shall always use the word in this sense hereafter) that the statement does not imply any law or fact*. It implies nothing about the laws or facts of measurement, except that these are of a certain form which is common to all such laws and facts; it cannot imply any other law, for the statement can be made when no laws except those of measurement are known. All the laws involving the numerical values of magnitudes are laws relating two or more numerical values.

We must now turn our attention to these laws, for on them depends derived measurement. The important question here is whether anything is altered in these laws by the change in the numerical values of fundamental magnitudes which is consequent on a change in the unit; for, if anything in the law is altered, or if by a change of units any law can become true which was previously false or *vice versâ*, then, and only then, does the choice of unit cease to be arbitrary. The question can be answered only if we are quite clear what these laws state. Suppose we are comparing the weight and the volume, both measured fundamentally, of different lots of water at 4°C . Then, if we adopt as our fundamental units the gram and the c.c., we shall find the law that the weight is always equal to the volume. If we adopt any other units, this law will not be true; but we shall have in its place the law that the weight is proportional to the volume, the constant of proportionality varying with the units. Now, is a law involving equality different from a law involving proportionality, or a law involving one constant of proportionality different from one involving another? If it is, then the law to be stated varies according to the fundamental units we adopt, and the choice of those units is not arbitrary; the choice determines the law. Perhaps Prof. Lewis or some other will say that laws of equality and of proportionality are different; let us examine the consequences of such a decision. The numerical law in question defines the derived magnitude density; if that law is not true, there is no such thing as the density of water at 4°C . If, then, the law is true when we choose one pair of units (A) and not when we choose another (B), water has a density in one case but not in the other. But now let us examine water at 0°C . According to the decision we have taken, water has no density if we choose the units A; for the relation

* The distinction between a fact and a law is discussed in 'Physics,' pp. 81-87.

between weight and volume is no longer equality; if we retain the same units, there can be no meaning in the statement that the density of a substance varies with its temperature. Such a statement has meaning only if we adopt one of two courses. Either we must admit that the law relating weight and volume, and therefore the meaning of density, is unaltered when the relation of proportionality is substituted for that of equality or the factor of proportionality otherwise changed; or we must measure every density in terms of different units, the numerical value of density being always the same. The second alternative is clearly fatal to Prof. Lewis's contention that there is one system of units preferable to all others on the ground that it removes arbitrary values; only the first (which, of course, is that universally adopted) need be considered. But if we adopt this first alternative, the law defining density will remain true whatever units we choose for measuring weight and volume; and we must conclude that in the statement of numerical laws and in derived measurement, so intimately connected with that statement, the choice of units is arbitrary in the sense that the truth or falsity of laws is unaffected by such choice. For exactly the same argument might be repeated for a numerical law involving numerical relations other than simple proportionality.

This, then, is our conclusion—it is trite enough. Whether we are speaking of fundamental or derived magnitudes, the statement that the magnitude characteristic of any system has one particular numerical rather than another is arbitrary; it does not imply a law or anything that is scientifically true. A law is implied in the statement that the magnitude is measurable; a law, or at least a fact, is implied in the statement that there is a numerical relation between one magnitude and another or, in particular, that a magnitude has a particular value in terms of stated units. But if anything beyond these statements is contained in the assertion of a particular numerical value, that something is not a scientifically significant proposition. And since change of units affects nothing but numerical values and leaves statements of the kind mentioned unaffected, any scientifically significant proposition which can be stated in terms of one set of units can be stated equally well in terms of any other. The choice of the units in which we state our laws will always remain arbitrary, unless the nature of those laws is profoundly changed.

8. So much for Prof. Lewis's presumption. I do not propose to examine his arguments; for that would lead us

into a discussion of the whole theory of dimensions, of which I have said enough elsewhere *. But to him, and to others who attempt to prove scientifically significant propositions by changing the dimensions conventionally attributed to derived magnitudes, I would suggest a dilemma. Either the statement that such a derived magnitude (*e.g.* velocity) has the conventional dimensions (*e.g.* lt^{-1}) is the expression of some scientific law or fact; or it is not. If it is such an expression then, unless the statement is actually untrue (a view not usually urged by those I am addressing), nothing true can be deduced by denying it. If it is not such an expression, but is a mere convention, then it is impossible to deduce from it anything scientifically significant, whether true or not.

9. Having contested so many of Prof. Lewis's assumptions and arguments, I cannot leave the matter without inquiring finally whether there is any grain among the chaff, and whether the facts to which he has drawn attention can be made the basis of any important conclusions. The new facts which he has brought to light are, so far as I can see, only two; namely that, within experimental error, $k^4 e^{-6} a^{-1} = (4\pi)^6$ and $(1/2 e^{12} k^{-3} c^{-6} = (4\pi)^{12} N^5$. Prof. Lewis says that it would be a "bizarre coincidence" if these numerical agreements were insignificant. Can we agree with him? I think this question can be answered if we return and ask once more: What are "simple" numbers, and why do we attach importance to them? †.

Prof. Lewis opens his paper (III) by speaking of "simple numbers like 2 and π ." It is clear, therefore, that in his view (in which I concur) physically simple is not the same thing as mathematically simple; for mathematically these numbers are almost as diverse as they can be: they resemble each other in nothing but being real. His view is more positively indicated in (I), where he argues that π is a simple number because it is important in geometry. If we ask why a number should be simple as a value for the electronic charge, because it is important in geometry, surely the only answer can be that it is simple because geometrical concepts are involved in all our laws and theories, whether they concern electrical or any other magnitudes. If this is so, the answer we must give to our questions is that values of magnitudes are simple when we hope or expect to be able to produce some law or theory to explain why the magnitudes have those values; and that the importance of simple numbers

* 'Physics,' Chs. xiv., xv.

† Cf. 'Physics,' pp. 431-434.

lies in the laws or theories which may explain them. That is the only answer I can find; and I am inclined to think that Prof. Lewis would accept it.

If we accept it, Prof. Lewis's contention that it cannot be a mere coincidence that $h^4 e^{-6} a^{-1}$ coincides so nearly in value with the simple number $(4\pi)^6$, and that therefore it must have exactly this value, should be interpreted to mean that he is confident that a theory can be produced (for a proposition connecting universal constants cannot be a law) to explain why $h^4 e^{-6} a^{-1}$ has this value, and that he is equally confident that none could be produced to explain why it has any other value lying equally within the range of experimental error of the measured value. But if this is his contention, it would be strengthened enormously if he could give some indication of what his theory is, and of why he is so sure that any theory leading to another value within the range is impossible. His position is entirely different from that of those who have produced actual theories which lead to numerical coincidences; it is infinitely weaker. And it is especially weak as regards its negative element: for the most surprising conclusions concerning simple numbers have turned out to be true. Thus, Planck's theory leads to the conclusion that $\frac{8\pi^5}{15}$ is a simple number in this sense, being involved in a theoretically explicable relation between universal constants*; while, on the other hand, since the relation which was at one time suggested, $\frac{(4\pi\epsilon)^2}{c} = \frac{h}{2\pi}$, turns out not to be true, $(4\pi)^2$ may not be a simple number. Probably we should all agree with Prof. Lewis if he asserted that some theory would be found some day which would connect together all of the universal constants between which no relation is known at present, and that this theory would introduce powers of π as a simple constant. But when he asserts that this constant must be $(4\pi)^6$ and no other (which does not differ greatly), he must pardon us if we do not share his confidence.

Lastly, if the day comes when such a theory is propounded, the theory of U.R.U. will at last be triumphantly established. For any set of units will give to all universal constants some values, and, whatever those values may be, they will be simple! The theory will be true,—but it will be useless.

Sept. 8, 1923.

* Prof. Lewis does not, or did not, accept Planck's theory (Phys. Rev. 4. 331, 1914). But he proposed an alternative theory to take its place; and this theory would presumably give the same value for the constant in the relation between a , h , k , c .

XV. *The Resistance of Air to Falling Spheres.* By
ROBERT G. LUNNON, M.A., M.Sc.*

I.

IT is well known that considerable disagreement exists as to the proper value of the constant ϕ_1 in the equation of fluid resistance for considerable speeds,

$$R = \phi_1 \rho d^2 v^2$$

where ρ is the fluid density, d the diameter (or some other length measurement) of the body, and v the uniform velocity. Results for spheres have been collected by Pannell † and by Schmidt ‡, and the values of ϕ_1 range from .08 to .28. A later value by L. F. Richardson § is .17, and another recent result, by Cooke ||, gives .24. These figures refer only to those relatively high speeds for which ϕ_1 is supposed to be constant. For lower values, ϕ_1 is usually compared with a second quantity of zero dimensions, the Reynolds number $\phi_2 = \nu d v^{-1}$, where ν is the kinematic viscosity, the quotient of the ordinary viscosity by the density. The proper form of the $\phi_1 \phi_2$ curve is also a matter of uncertainty (see Pannell's report ¶ and the Enc. of App. Physics, vol. i. p. 369). Further, the conditions with non-uniform velocities have been examined only by Schmidt **, for low velocities, except for certain data recorded by Allen †† and by Shakespear ‡‡. The measurements to be recorded in this paper were made with the object of obtaining more light on these three problems.

II.

Measurements have been made of the times of fall of spheres of various sizes and densities for distances up to 600 metres in the shafts of four coal-mines in this district, and also, for shorter distances, in the tower and laboratories of this College. In the mine-shafts the balls were released by an assistant in the cage, which was set at different heights for successive experiments, and were received in a suitable truck or enclosed space at the shaft bottom. In some cases

* Communicated by the Author.

† Pannell, Adv. Ctee. for Aeronautics, Report No. 190 (1914).

‡ Schmidt, *Ann. der Physik*, lxi. p. 633 (1920).

§ L. F. Richardson, *Phil. Trans. A*, 223, p. 351 (1923).

|| Cooke, *Phil. Mag.* xxxix. p. 350 (1920).

¶ *Loc. cit.*

** *Loc. cit.*

†† Allen, *Phil. Mag.* l. pp. 323, 519 (1900).

‡‡ Shakespear, *Phil. Mag.* xxviii. p. 728 (1914).

the times of release and of striking were recorded by electromagnetic arrangements similar to those described by Shakespear*, with the addition of a tape-machine or a chronograph. More often, in the pits, the release alone was electromagnetic, and the time of striking, as heard, was measured by a special stop-watch. In a few cases the ball was dropped by hand and the time of release signalled by sound to the recorder below, a correction being then made for the speed of sound. Usually five balls of the same size were dropped consecutively, and from the concordance of their times, and also of the times in different pits, after allowance for air-currents, it appeared that the errors did not exceed one-fiftieth of a second for times up to 6 seconds, and one-tenth for times up to 15 seconds. Some of the conditions in the pits were particularly difficult, and this degree of exactness was considered satisfactory.

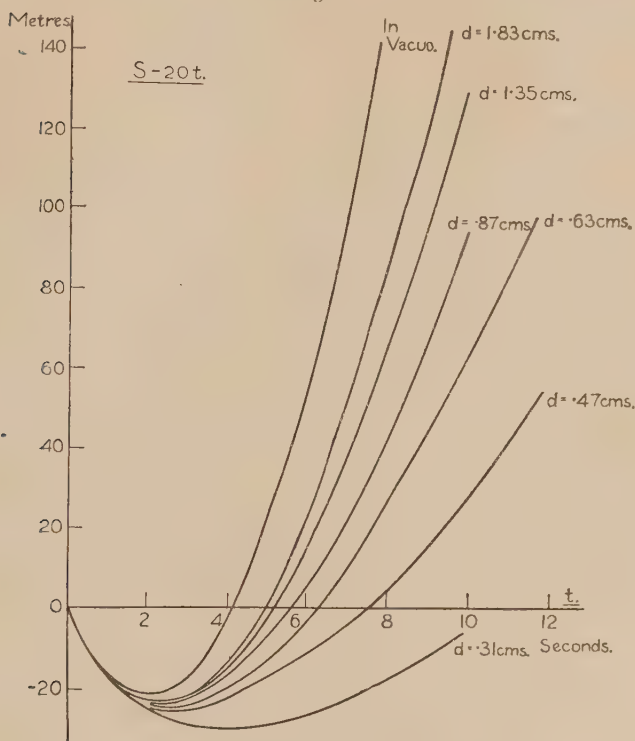
Polished steel balls were chiefly used for the experiments. These were of fifteen different sizes, varying from 0.24 cm. to 1.83 cm. in diameter, and were of density 7.72 grams per cm.³: the actual measurements are recorded in Table III. The corrected results for the relation between time of fall and distance are given in fig. 1 and in Table II. These refer to a few of the sizes only, for the sake of simplicity, and the results for the remaining sizes may be easily calculated from the formula given hereafter. The actual distances through which the falls were timed were (in metres) 568, 456, 346, 115, 88, 49 in pit W, 320 in pit H, 309, 247, 181, 117, 62 in pit U, 126, 110, 92, 73.5, 55.2, 35.1, 17 in pit B, and several distances less than 25 metres in the College buildings. Some 500 measurements in all have been used in obtaining the figures of Table II. and the graphs of fig. 1. It is to be noticed that fig. 1 does not show the relation between distance (s) and time (t) directly, for the (s, t) curves are not clearly separable on any convenient scale. It is convenient to plot $s - 20t$, where s is in metres, against t , and the values of s for any given values of t may easily be calculated after a reading of the graph.

In the results thus shown, the actual observations are not given, but their values corrected for standard conditions. The chief correction is that needed on account of the air-currents in the pit-shafts. These troublesome currents cannot be avoided, for forced ventilation is continuous in most mines, and even when the driving-fan can be stopped, there is a certain amount of natural draught. It was

* *Loc. cit.*

generally possible to work in sections in which the draught was uniform, and after taking anemometer measurements in each case, corrections could be made according to the theory which is developed later. These corrections were small, except for the smallest balls; and this is fortunate, because their calculation involves certain empirical constants which

Fig. 1.



can only be determined approximately from the actual results. The measurements over the longest distances, in pit W, were useless because of the great speed and non-uniformity of the air-draught, and it is hoped to repeat these elsewhere.

III.

The equation of motion for a falling sphere is

$$m\dot{v} = mg - R,$$

and if $R = \phi_1 \rho d^2 v^2 = av^2$, say, then

$$m\dot{v} = mg - av^2. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Integrating, and putting $v=0$ when $t=0$, leads to

$$v=c\left[1-\frac{2}{1+e^{pt}}\right]=c \tanh pt,$$

where

$$c=\sqrt{\frac{mg}{a}}, \quad p=2\sqrt{\frac{ag}{m}}. \quad (2)$$

This is easily integrated, and leads to

$$\begin{aligned} s &= \frac{2c}{p} \log \frac{1+e^{pt}}{2} - ct \\ &= \frac{2c}{p} \log \cosh \frac{pt}{2} \quad \text{or} \quad \frac{m}{a} \log \cosh \frac{pt}{2}. \quad (3) \end{aligned}$$

This formula is a cumbrous one for computation, but it has the advantage that it can be compared directly with the s, t data. Many workers have preferred to deduce the velocity from their results, and even the acceleration, but there is a risk of serious error in these deductions, and we have preferred the longer method. It was found after trial of a succession of values of c and p , that it was possible to obtain a good fit of the experimental curves with formula (3). But whereas the values of c —the terminal velocities—were proportional to $\sqrt{\frac{m}{a}}$ for different balls, as (2) indicates, the

values of p were not inversely proportional to this, as in (2).

Schmidt has proposed to amend equation (1) by assuming that when v is not uniform the resistance depends upon the acceleration in this manner:

$$R=av^2+b\dot{v}-k\dot{v}^2.$$

For a special value of the constant k , this leads to an integrable form of the equation of motion, with the result

$$v=c(1-e^{-qt}),$$

and hence to

$$s=ct-cq^{-1}(1-e^{-qt}).$$

This result does not fit our experimental data better than (3), and although it offers simpler formulæ for v and s , it only does so after a special assumption.

We have therefore considered a rather simpler hypothesis, viz. that

$$R=av^2+b\dot{v}, \quad (4)$$

where the constant b , like a , is proportional to the area of

the ball. This leads to the same form as the simple square law,

$$s = \frac{2c}{p} \log \frac{1 + e^{pt}}{2} - ct,$$

but in this the value of p is changed :

$$c = \sqrt{\frac{mg}{a}}; \quad p = \frac{2\sqrt{amg}}{m+b}, \quad \dots \dots (5)$$

and s may now be written

$$s = \frac{m+b}{a} \log \cosh \frac{pt}{2}. \quad \dots \dots (6)$$

The connexion between c and p is here of the form

$$p^{-1} = Ac + Bc^{-1}.$$

This relation was found to hold for the values of p and c which best fitted the experimental results, and the hypothesis (4) is therefore justified. By taking the best values for a and b , the values of p and c have been deduced for each size of ball, and formula (6) provides the means for an exact comparison of theory and experiment.

It is first necessary, however, to examine the important air-current corrections. When a ball falls against an upward current of air of n cm. per second, equations (1) and (4) must be replaced by

$$m\dot{v} = mg - a(v+n)^2 - b\dot{v},$$

and the solution of this is

$$s = \frac{2c}{p} \log \frac{1 + re^{pt}}{1+r} - (c+n)t, \quad \dots \dots (7)$$

where

$$r = \frac{c+n}{c-n}.$$

When the current is downward, it helps the ball until $v=n$, and for this period,

$$m\dot{v} = mg + a(n-v)^2 - b\dot{v},$$

from which there follows

$$v = n - c \left[\frac{n - c \tan \frac{pt}{2}}{c - n \tan \frac{pt}{2}} \right].$$

Hence $v=n$ when $c \tan \frac{1}{2} \rho t = n$; and since n is small compared with c , we may write from this, $t = \frac{2n}{pc} = T$, say. In our experiments, T was always less than one second, and the distance travelled in this time is found, by a further approximate integration, to be $s = \frac{n^2}{pc} = S$, say.

The further motion follows the law

$$m\dot{v} = mg - a(v-n)^2 - b\dot{v}.$$

This may easily be solved, and finally we obtain for the total distance fallen,

$$s = \frac{2c}{p} \log \frac{1 + e^{pt'}}{2} - (c-n)t' + S, \quad \dots (8)$$

where $t' = t - T$, and c, p have the same meanings as before.

The expressions (6), (7), and (8) cover all the cases of our experiments. The effect of the wind, as calculated from these equations, may be seen from the following figures, referring to a steel ball of 1.11 cm. diameter for which $c = 5090$ cms. per sec., $p = .343$. They give the distances fallen in stated times—first, in still air; second, against a current of 1.8 metres per second; and third, with a current of 4.8 metres per second; these were the actual currents in two of the pits.

TABLE I.

Times of fall	2	4	6	8	10	12 seconds.
In still air	17	65	134	220	312	410 ..
Against 1.8 m.p.s.	165	64	132	214	303	398 ..
With 4.8 m.p.s. ...	18	66	140	238	333	443 ..

It was found that the corrections based on these figures made a satisfactory concordance between the results of the four pits for those distances which they had in common.

The conditions of fall vary also in respect of air-density and of the strength of gravity. The variation of g with depth, as measured approximately by Airy's experiments in the neighbouring Harton pit, is much too small to affect the present results. As regards density, there was an increase in temperature of 9°C. and in pressure of 82 millibars at the bottom of the deepest shaft, and also the humidity had increased to saturation. Measurements were made in each case, and the maximum variations led to a 4 per cent. increase in density (at 600 metres), and hence to a reduction of 2 per cent. in c . It is not possible to state exactly the

effect upon the second constant p , because this depends upon b , of which the nature is unknown*. But the effect of b is small except for the smallest balls, and, apart from this, we find an increase in p of 2 per cent. for a ball of .87 cm. in diameter. These changes in c and p together, only produce an appreciable change over long distances: their effect would be to reduce the distance travelled in 10 seconds from 298 to 295 metres. The actual corrections which have been made in the following figures in no case exceed two metres.

The complete data for falling spheres in dry air at normal temperature and pressure are set out in the following table. Besides the figures derived from the experiments, there are the distances in smaller type which have been calculated from the theory.

TABLE II.

Table of Distances fallen in stated times.

Diameter...	.317 cm.	.476	.635	.873	1.110	1.349	1.650	1.826	
Mass	129 gm.	.432	1.03	2.69	5.54	9.93	18.2	24.6	
Terminal velocity (c)	} 27.1	33.1	38.3	45.0	50.9	55.8	61.8	65.1	metres per second.
p51	.461	.422	.378	.343	.319	.293	
Distances travelled, in metres.									
1 second	4.3	4.4	4.5	4.6	4.6	4.7	4.8	4.90
	3.3	3.5	3.7	4.0	4.1	4.2	4.2	4.2	
2 seconds...	16	16.2	16.5	17	17	17.5	...	18.7	19.6
	13	14.5	15.5	16	17	17			
4 " ...	50	59	62	64	65	67	...	68	78
	47	54	58	62	65	67	68.5	69	
6 " ...	94	110	117	128	132	135	139	145	176
	92	107	117	128	134	139	144	147	
8 " ...	142	166	186	204	...	226	243	...	312
	143	167	186	206	220	231	243	245	
10 " ...	194	228	265	295	312	327	347	...	490
	197	232	260	290	312	330	347	356	
12 "	297	343	707
	...	298	337	378	410	438	466	476	

It will be seen that the fit of experiment and formula is a good one within the range of sizes and times dealt with. The chief divergences occur at the shorter periods, for which the present theory is not expected to be applicable. For very low speeds the resistance must follow Stokes's law; and after this stage is passed, the s, t curve must show at least one

* The dimensions of b suggest its dependence upon the volume, rather than upon the area, of the ball; but it is important to notice that the experimental results lend no support to this view.

double bend, as Schmidt's results very well show, when the first vortex ring forms and slips off behind the ball. No evidence of these initial stages can be expected from the present experiments, for they are probably completed during the first few centimetres of fall. No single formula can represent the passage of the sphere from the stage of steady, slow motion, through that which produces steadily increasing turbulence in the air, up to the final stage of "steady" turbulence. The formula we have considered is also inapplicable at the commencement of fall, because it assumes an initial acceleration of $\frac{m}{m+b} \cdot g$ instead of g ; for our equation of motion may be written thus:

$$(m+b)\dot{v} = mg - av^2.$$

The constant b appears to represent a "dragged" mass, adding to the inertia but not to the gravitational pull; but its magnitude, $\cdot 55d^2$, is much greater than can be explained on a physical basis of this kind.

The values of the constants which are found to give this best fit of experiment and formula are

$$c = \frac{2400\sqrt{m}}{d}; \quad p = \frac{2gc}{c^2 + 3,170,000},$$

and hence, from (5),

$$a = 1.70 \times 10^{-4}d^2, \quad b = \cdot 55d^2.$$

The constant a is often written $\phi_1\rho$, as above; and introducing $\rho = \cdot 00129$, we find for the resistance

$$R = \underline{\cdot 132\rho d^2 v^2 + \cdot 55d^2 \dot{v}}.$$

These figures refer throughout to C.G.S. units, and numerical values for c , p , and b are given in Table III.

The new value of ϕ_1 , viz. $\cdot 132$, holds for velocities from 25 to 65 metres per second, and for values of ϕ_2 between 5000 and 85,000; it is estimated to be correct within 4 per cent. It may be compared with the values $\cdot 130$ to $\cdot 150$ found by Allen for similar balls falling in water, with $\cdot 170$ found by Schmidt for lighter spheres in air and water, and with the range $\cdot 165$ to $\cdot 188$ found by Shakespear for larger and lighter balls in the air. These last results are in rough accord with our own, for Shakespear found a decrease in ϕ_1 for diminishing diameters, and an extrapolation of his formula leads to values of ϕ_1 between $\cdot 13$ and $\cdot 14$ for diameters of

a centimetre. The present experiments, however, showed no sign of variation with diameter between $d=0.4$ and $d=1.8$ cm.

TABLE III.

Diameter (cm.).	Mass (grams).	c (terminal velocity) (cm. per sec.).	p (sec. ⁻¹).	b (grams).
·238	·054	2350	·54	·031
·317	·129	2710	·51	·055
·476	·432	3310	·461	·124
·555	·692	3590	·439	·169
·635	1·03	3830	·422	·22
·714	1·47	4070	·406	·28
·873	2·69	4500	·378	·42
·952	3·48	4700	·366	·50
1·03	4·44	4900	·354	·58
1·11	5·57	5090	·343	·68
1·35	9·89	5580	·319	1·00
1·55	15·16	5970	·301	1·32
1·65	18·25	6180	·293	1·50
1·83	24·67	6510	·280	1·83

There is little basis for a comparison of the new acceleration term with the results of other workers. Shakespear deduced from his experiments that if different balls fall a certain distance in the same time, then their weights are proportional to their areas. This is in agreement with our theory; for from (5), in which a and b are proportional to the areas, it may be shown that c and p are constants if this relation holds.

The only result published by Allen for non-uniform velocities refers to a ball falling in water. With the constants in question, $d=0.318$ cm., $m=0.132$ gram, our theory gives the terminal velocity, c , as 91.9 cm. per sec., whereas Allen found 90.9 by experiment. To find p , we substitute the effective weight, in water, for the actual weight, in the numerator of (5), and since the dimensions of p are [time]⁻¹, no further change is needed. Calculation gives $p=13.1$; and the theoretical curve obtained from these values of c, p is an excellent fit for Allen's measurements, as recorded.

It may be noted in conclusion that the present theory answers a question raised by Shakespear. If two spheres of different diameters are weighted so as to fall a certain distance in equal times, will they take equal times for all

other distances? We have seen that for two such balls the ratio of mass to area is the same, and hence the constant ρ can be expressed in terms of c :

$$\rho = \alpha c (\beta + c^2)^{-1}.$$

The equation of motion may therefore be written in the form

$$s = \frac{2}{\alpha} (\beta + c^2) \left[\log \left(1 + c^{\frac{\alpha c t}{\beta + c^2}} \right) - \log 2 \right] - ct,$$

and the question asked is whether the same pair of values of s and t could occur for different values of c . It seems that the members of the family of s, t curves obtained by varying c do not intersect within the region of positive values of s and t ; and we conclude that the value of c is uniquely determined by one pair of s, t values. Hence, if two balls are together at one point of their fall, after starting together, they remain together throughout.

The author's thanks are due to the managers of the Blucher, Wearmouth, Usworth and Hebburn Pits for their kindness in offering facilities and considerable help for these experiments, and to Mr. L. F. Richardson for some useful comments upon the work.

Summary.

1. The fall of small steel balls in coal-mine shafts has been investigated, and results are given, corrected, for dry, still air.
2. A value $\phi_1 = 132$ is obtained for the resistance coefficient for steady motion, for values of ϕ_2 , the Reynolds number, from 5000 to 85,000.
3. For accelerated motion, the formula

$$R = \phi_1 \rho d^2 v^2 + b \dot{v}$$

is introduced, and found to give satisfactory results after the first 2 seconds, the value of b being $\underline{.55d^2}$ in C.G.S. units, d being the diameter in centimetres.

Armstrong College,
Newcastle-on-Tyne.
Sept. 3rd, 1923.

XVI. *On Waves due to a Single Impulse in Deep and Shallow Water.* By GEORGE GREEN, D.Sc., *Lecturer in Natural Philosophy in the University of Glasgow* *.

THE problem of determining the wave-motion due to an initial surface elevation confined to the immediate neighbourhood of any point is fully discussed in Lamb's 'Hydrodynamics' for the case of infinitely deep water. The corresponding problem for the case of finite depth is treated by the late Lord Rayleigh in "On the Instantaneous Propagation of Disturbance in a Dispersive Medium, exemplified by Waves on Water Deep and Shallow" (Phil. Mag. xviii. 1909). The aim in view in this paper is to trace the effect of increase of depth on the wave-motion arising from a specified initial disturbance. Lord Rayleigh points out that certain gaps exist in our solutions, and that some transformation of the fundamental integral is called for. The fundamental integral has since been evaluated in the form of a convergent series by Pidduck †. In the present paper the intention is to indicate a transformation of the fundamental integral which overcomes the difficulty pointed out by Lord Rayleigh, and to discuss more fully the formation of the front for the case of waves advancing in shallow water. Professor Lamb, referring to the problem for deep-water waves, points out its value in extending our knowledge of the whole process of wave propagation in dispersive media. The corresponding problem for shallow-water waves has an added interest in this connexion, as it illustrates the case, not yet investigated, where the wave-velocity and group-velocity are finite for all wave-lengths, this being the case most frequently met with in optics ‡. This paper is also intended especially to illustrate the extended application of the principle of stationary phase outlined in a recent paper §.

According to Fourier's theorem the displacement, ξ , at any point of the free surface at time t , arising from an initial elevation confined to the immediate neighbourhood of the origin, is expressed by

$$\xi = \frac{1}{\pi} \int_0^{\infty} dk \cos kx \cos \sigma t, \quad \text{where } \sigma = kV = (gk \tanh kh)^{1/2}. \quad (1)$$

In the above, h represents the uniform depth of the fluid,

* Communicated by the Author.

† Proc. Roy. Soc. vol. lxxxiii. p. 347 (1910).

‡ Phil. Mag. vol. xxxix. pp. 653-659 (June 1920).

§ Phil. Mag. vol. xlv. pp. 1156-1167 (June 1923).

and V represents the wave-velocity corresponding to wave-length $\frac{2\pi}{k}$. As stated by Lord Rayleigh, the difficulty in the evaluation of the integral lies in the fact that, as written above, it is divergent. Similarly, in the equivalent expression,

$$\xi = \frac{1}{2\pi} \int_0^\infty dk \cos(kx - \sigma t) + \frac{1}{2\pi} \int_0^\infty dk \cos(kx + \sigma t), \quad (2)$$

both integrals are divergent; but these integrals can each be transformed into two integrals, one of which is divergent and the other convergent, by the method indicated in the equation

$$\begin{aligned} \int_0^\infty dk \cos(kx - \sigma t) &= \frac{1}{x} \int_0^\infty dk \left(x - \frac{d\sigma}{dk} t \right) \cos(kx - \sigma t) \\ &+ \frac{t}{x} \int_0^\infty dk \frac{d\sigma}{dk} \cos(kx - \sigma t). \quad \dots \quad (3) \end{aligned}$$

If in the first term on the right we put $k'x = kx - \sigma t$, the integral becomes $\int_0^\infty dk' \cos k'x$, which, according to Fourier's integral theorem, represents a quantity which is zero at all points except at $x=0$. We can accordingly evaluate ξ from the expression

$$\begin{aligned} \xi &= \frac{t}{2\pi x} \left[\int_0^\infty dk \frac{d\sigma}{dk} \cos(kx - \sigma t) - \int_0^\infty dk \frac{d\sigma}{dk} \cos(kx + \sigma t) \right] \\ &= \frac{t}{\pi x} \int_0^\infty dk \frac{d\sigma}{dk} \sin kx \sin \sigma t, \quad \dots \quad (4) \end{aligned}$$

provided we exclude the origin. The integrals obtained in (4) are in general convergent.

The application of (4) to the case of infinitely deep water ($\sigma^2 = gk$) gives

$$\begin{aligned} \xi &= \frac{g^{1/2} t}{4\pi x} \left[\int_0^\infty dk k^{-1/2} \cos(kx - \sigma t) \right. \\ &\quad \left. - \int_0^\infty dk k^{-1/2} \cos(kx + \sigma t) \right], \quad \dots \quad (5) \end{aligned}$$

and it is easy to verify that this leads to the well-known result given by Prof. Lamb. If we make the substitutions $v = c^{1/2} \left(k^{1/2} - \frac{g^{1/2}t}{2c} \right)$ in the first integral in (5), and $v = c^{1/2} \left(k^{1/2} + \frac{g^{1/2}t}{2c} \right)$ in the second, the expression then becomes

$$\xi = \frac{g^{1/2}t}{2\pi c^{3/2}} \int_{-\omega}^{+\omega} dy \cos \left(y^2 - \frac{gt^2}{4x} \right), \quad \text{where} \quad \omega^2 = \frac{gt^2}{4x}, \quad (6)$$

which is equivalent to the result contained in equation (23) of Prof. Lamb's address*.

A similar application of (4) to the case of water of finite depth h gives the result

$$\begin{aligned} \xi = \frac{g^{1/2}t}{4\pi x} & \left[\int_0^\infty dk \tanh^{1/2} kh k^{-1/2} \{ \cos(kx - \sigma t) - \cos(kx + \sigma t) \} \right. \\ & \left. + h \int_0^\infty dk \tanh^{-1/2} kh \operatorname{sech}^2 kh k^{1/2} \{ \cos(kx - \sigma t) - \cos(kx + \sigma t) \} \right] \\ \text{or} & \quad \quad \quad . \quad . \quad . \quad (7) \end{aligned}$$

$$\begin{aligned} \xi = \frac{g^{1/2}t}{2\pi x} & \left[\int_0^\infty dk \tanh^{1/2} kh k^{-1/2} \sin kx \sin \sigma t \right. \\ & \left. + h \int_0^\infty dk \tanh^{-1/2} kh \operatorname{sech}^2 kh k^{1/2} \sin kx \sin \sigma t \right], \quad . \quad . \quad . \quad (8) \end{aligned}$$

in which $\sigma^2 = gk \tanh kh$.

When h becomes exceedingly great the first integral in (7) or (8) tends to the value of ξ given in equation (5), while the second integral tends to zero. The difference between the displacements at any instant, corresponding to infinite and finite depth respectively, is accordingly indicated clearly by equations (5), (7), (8).

The evaluation of ξ for any assigned depth, however small, can now be carried out by means of equation (8). By expanding $\sin \sigma t$ and integrating term by term we obtain a convergent series which has been already given

* Presidential Address, London Math. Soc. 1904.

by Pidduck. Its first term is given by

$$\begin{aligned} T_1 &= \frac{gt^2}{2\pi x} \left[\int_0^\infty dk \tanh kh \sin kx + h \frac{d}{dh} \int_0^\infty dk \tanh kh \sin kx \right] \\ &= \frac{gt^2}{2\pi x} \left[\left(1 + h \frac{d}{dh} \right) \left(\frac{\pi}{2h} \operatorname{cosech} \frac{\pi x}{2h} \right) \right] \\ &= \frac{gt^2 \pi}{8h^2} \cosh \left(\frac{\pi x}{2h} \right) / \sinh^2 \left(\frac{\pi x}{2h} \right). \quad \dots \dots \dots (9) \end{aligned}$$

The second term is given by

$$\begin{aligned} T_2 &= \frac{2!}{4!} \frac{gt^2}{dh} \frac{dT_1}{dh} \\ &= -\frac{g^2 t^4 \pi}{384 h^4} \left\{ 4h \sinh \frac{\pi x}{h} - \pi x \left(3 + \cosh \frac{\pi x}{h} \right) \right\} / \sinh^3 \frac{\pi x}{2h}. \quad \dots \dots \dots (10) \end{aligned}$$

These values for the first two terms of the series are given by Pidduck. All the higher order terms in succession can be obtained from these by means of the equation

$$T_n = -\frac{(2n-4)!}{2n!} g^2 t^4 \frac{dT_{n-2}}{dx^2} + \frac{1}{(n-1)} \cdot \frac{(2n-2)!}{2n!} g t^2 \frac{dT_{n-1}}{dh}. \quad \dots \dots \dots (11)$$

In this way it is easy to derive the terms, but as the series converges very slowly at first and is only suitable for calculation when t is small, it is unnecessary to give the terms in full.

The values of the first six terms of the series, corresponding to the conditions $t = 1$ second and $h = 2$ feet, are shown in the accompanying table for values of x from

x .	T_1 .	T_2 .	T_3 .	T_4 .	T_5 .	T_6 .	ξ .
4	·272	·413	-·764	·171	+·102	-·050	·15
5	·124	·318	-·311	-·024	+·073	-·019	·162
6	·056	·204	-·104	-·058	+·039	-·005	·135
7	·026	·120	-·016	-·045	+·015	+·0001	·100
8	·012	·067	+·0119	-·027	+·0046	+·0011	·069
9	·0054	·036	+·0164	-·014	+·0003	+·0009	·045
10	·0024	·019	+·0136	-·0062	-·0009	+·00057	·028

4 to 10. In the calculation of these terms the approximate expressions for the successive terms, indicated by

$$T_1 = \frac{gt^2 \pi}{4h^2} e^{-\frac{\pi x}{2h}} \quad \dots \dots \dots (12)$$

for the first term, have been employed. The approximation is very close from $x = 5$ onwards, and at $x = 4$ the error in the value obtained for ξ arising from the use of the approximate expressions is about four per cent. To obtain the value of ξ at time $t = 1$ second corresponding to any value of x less than 4 we should require to use the exact values of the terms. The series indicated above, with the numerical values of the terms given in the table, would be useful for all values of t less than unity, but the labour involved in calculating the value of ξ by means of the above series when t exceeds unity would be much too great. We shall now show that the calculation can be carried out much more simply for all values of t greater than unity by an entirely different method, depending on the principle of stationary phase treated in my former paper*.

In the expression (2), the displacement ξ appears as the resultant effect due to two systems of wave-trains moving in opposite directions. In considering the displacement at any point for which x is positive we may take

$$\xi = \frac{1}{2\pi} \int_0^{\infty} dk \cos(kx - \sigma t), \quad \sigma = (gk \tanh kh)^{1/2}, \quad (13)$$

in which only positive values of k are considered. The omitted integral we shall deal with later on. This integral in (13) is similar to that discussed in the paper above referred to. At any point x at time t the phase-curve is a curve with two stationary points, one at a positive and one at a negative value of k , and the point of inflexion is at $k=0$. At any time t the points of stationary phase for all points near the front of the wave-system correspond to very small values of k , and an exceedingly close approximation to the true value of ξ is then given by

$$\xi = \frac{1}{2\pi} \int_0^{\infty} dk \cos \left[k(x - \sqrt{gh}t) + \frac{k^3}{6} \sqrt{gh^5}t \right] \quad (14)$$

or by

$$\xi = \frac{1}{2\pi} \cdot \left(\frac{3\pi}{\sqrt{gh^5}t} \right)^{1/3} \int_0^{\infty} dz \cos \frac{\pi}{2} (z^3 - mz), \quad (15)$$

where

$$m = \frac{2}{\pi} \left(\frac{3\pi}{\sqrt{gh^5}t} \right)^{1/3} (\sqrt{gh}t - x).$$

The value of the above integral, for positive or negative

* Phil. Mag. (June 1923).

values of m , has been obtained in terms of the Bessel's Functions, $J_{1/3} \left\{ \pi \binom{m}{3}^{3/2} \right\}$ and $J_{-1/3} \left\{ \pi \binom{m}{3}^{3/2} \right\}$. Numerical values have also been given by Airy for the range $m = -5.6$ to $+5.6$. The above evaluation is valid for all negative values of m and for positive values subject to the condition that

$$k_1^2 = \frac{2(\sqrt{gh}t - x)}{\sqrt{gh^5}t} = \text{a very small quantity,} \quad (16)$$

k_1 being the value of k positive for which the phase is stationary at point x at time t . This condition excludes all values of x small compared with $\sqrt{gh}t$, and it also excludes large values of m unless t also is very large compared with $(\sqrt{gh}t - x)$. In the immediate neighbourhood of the point $x = \sqrt{gh}t$ the above is valid over a very large range of t . At $t = 1$ second, $x = 8$, the above integral gives for ξ the value .070 as against .069 obtained by the previous calculation by means of the series. The limitation expressed by (16) above renders the expression (14) invalid for values of k greater than about .1 in the case of a wave-disturbance in shallow water. But (14) is of considerable importance in relation to dispersion in general. It represents a wave-disturbance advancing in any medium which is only slightly dispersive, being applicable to all substances to which Cauchy's law of dispersion applies*.

The principle of stationary phase may be applied to evaluate (13) without the limitation referred to above. The true phase curve for (13) may be written in the form

$$\phi(k) = \sqrt{\frac{g}{h}} \cdot t \cdot z \left(\alpha - \frac{\tanh^{1/2} z}{z^{1/2}} \right), \text{ where } z = kh \quad (17)$$

and α represents $x/(\sqrt{gh}t)$. We then have

$$\begin{aligned} \frac{d\phi}{dk} &= \sqrt{gh} \cdot t \left\{ \alpha - \frac{1}{2} \frac{\tanh^{1/2} z}{z^{1/2}} - \frac{1}{2} \frac{z^{1/2}}{\tanh^{1/2} z} + \frac{1}{2} z^{1/2} \tanh^{3/2} z \right\} \\ &= \sqrt{gh} \cdot t \{ \alpha - F(z) \}, \quad (18) \end{aligned}$$

$$\frac{d^2\phi}{dk^2} = -\sqrt{gh^3} \cdot t \cdot F'(z), \quad \text{and} \quad \frac{d^3\phi}{dk^3} = -\sqrt{gh^5} t F''(z). \quad (19)$$

The phase curve is only required for positive values of z .

* A diagram of the integral contained in (15) for small values of m is given in a paper on Ship-Waves by Hogner, *Arkiv för Matematik, Astronomi och Fysik*, Band xvii. No. 12 (1923).

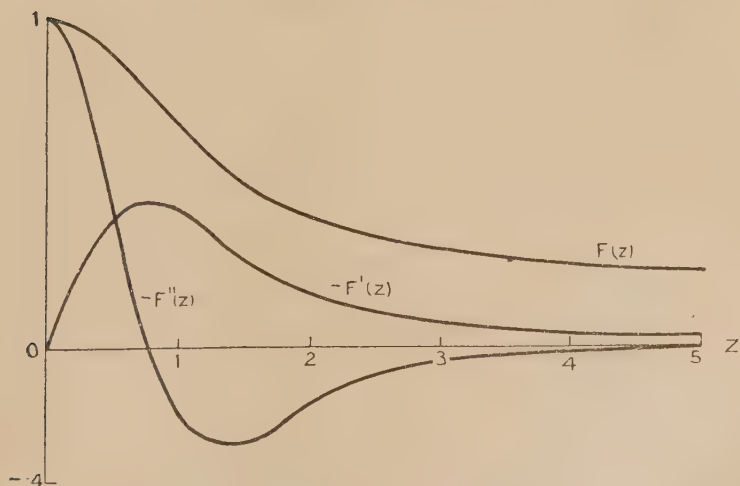
It has a point of inflexion at the origin and a zero at the point defined by $\alpha^2 = \tanh z/z$, provided α is less than unity. Between the origin and this point, at k_0 say, there is a point of stationary phase at which $\alpha = F(z)$. The method to be used in the evaluation of ξ consists in replacing the true phase curve by an auxiliary phase curve, which is in close agreement with the true phase curve at the point k_0 , and for a range on either side of k_0 . In the notation employed in my former paper, the auxiliary phase curve, at point x at time t , is that represented by

$$\phi_1 = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3, \quad \dots \quad (20).$$

where $a = \phi(k_0)$, $b = \phi''(k_0)$, $c = \phi'''(k_0)$, and $\sigma = (k - k_0)$.

For values of z exceeding $z=4$, $\tanh z=1$, and the phase curve practically coincides with the phase curve for the case of infinitely deep water. This range of values of z or $k_0 h$ corresponds with small values in α or $x/(\sqrt{gh}t)$ and for these values of x and t the displacement curve is nearly the same for infinitely deep water and for shallow water of any assigned depth. As the displacement in infinitely deep water corresponding to our initial displacement is fully

Fig. 1.



determined by the investigations of Professor Lamb, we require to investigate the displacement corresponding to the range of values of z from zero to four.

In figure 1 the diagrams represent $F(z)$, $-F'(z)$, and $-F''(z)$ respectively so that the values of b and c required.

in (20) can be read direct from these curves with the correct sign indicated by the diagram. The method of using these curves is as follows :— For any assigned α find z_0 to fulfil the condition $\alpha = F(z_0)$, then with this value of z in (17) calculate $\phi(k_0)$ or a , and with the same value of z find b and c from the curves in figure 1. From the values of a, b, c , so found, the auxiliary phase curve at x at time t is determined. The auxiliary phase curve determined in this way varies in type for different values of z . Thus for any value of z from zero to $\cdot 76$, b and c are both positive and the general shape of the curve is similar to that of the true phase curve over the full range of k from 0 to x . In this range of z , therefore, the auxiliary curve can be employed for integration over the full range of k from 0 to ∞ . For example, with

$$x/(\sqrt{gh}t) = \cdot 875, \quad h=2, \quad t=1, \quad z_0 = k_0 h = \cdot 53, \quad a = -\cdot 0435 \sqrt{\frac{g}{h}} t$$

$$b = \cdot 401 \sqrt{gh^3} t, \quad c = \cdot 350 \sqrt{gh^5} t, \text{ and}$$

$$\xi = \frac{1}{2\pi} \int_{-k_0}^{\infty} d\sigma \cos \left\{ a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 \right\}. \quad (21)$$

If we transfer the origin to the point of inflexion on the auxiliary phase curve, by the substitution $w = \left(\frac{c}{3\pi}\right)^{1/3} \left(\sigma + \frac{b}{c}\right)$, the above expression becomes

$$\xi = \frac{1}{2\pi} \left(\frac{3\pi}{c}\right)^{1/3} \int_{\rho}^{\infty} dw \cos \left\{ \left(a + \frac{1}{3} \frac{b^3}{c^2}\right) + \frac{\pi}{2} (w^3 - mw) \right\}, \quad (22)$$

where $\rho = \left(\frac{c}{3\pi}\right)^{1/3} \left(\frac{b}{c} - k_0\right)$, and $\pi \left(\frac{m}{3}\right)^{3/2} = \frac{1}{3} \frac{b^3}{c^2}$. The integrals

$$\int_0^{\infty} dw \cos \left\{ \frac{\pi}{2} (w^3 - mw) \right\} \quad \text{and} \quad \int_0^{\infty} dw \sin \left\{ \frac{\pi}{2} (w^3 - mw) \right\}$$

have been evaluated in the paper already referred to, and the integrals

$$\int_0^{\rho} dw \cos \left\{ \frac{\pi}{2} (w^3 - mw) \right\} \quad \text{and} \quad \int_0^{\rho} dw \sin \left\{ \frac{\pi}{2} (w^3 - mw) \right\}$$

are easily evaluated by quadratures for small values of ρ . In this way, at $t=1$ second, $x=7$, the value obtained for ξ is $\cdot 101$ as against $\cdot 100$, the value given by the convergent series in the table on page 186, thus proving that the above evaluation is valid up to $z = \cdot 53$ from $z=0$.

In the neighbourhood of $z=0.76$ the type of the auxiliary curve changes owing to the vanishing of c . Thus, with

$$x/(\sqrt{gh}t)=0.75, \quad z_0=k_0h=0.83, \quad a=-0.1295\sqrt{\frac{g}{h}}t,$$

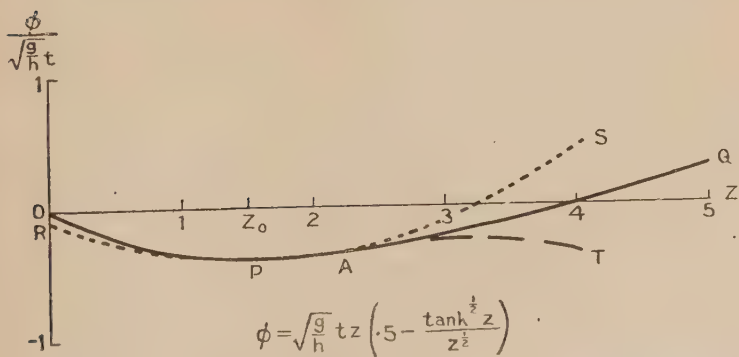
$b=0.436\sqrt{gh^3}t$, c =a very small negative quantity.

Since c is negative, the auxiliary phase curve (20) differs in type from the true phase curve beyond the point of inflexion on the auxiliary curve, which, therefore, cannot be used to replace the true phase curve over the full range of k . As c is small, however, a very close approximation to the value of the displacement is given by

$$\begin{aligned} \xi &= \frac{1}{2\pi} \int_{-k_0}^{\infty} d\sigma \cos \left\{ a + \frac{b\sigma^2}{2!} \right\} \\ &= \frac{1}{2(2\pi b)^{1/2}} \cos \left(a + \frac{\pi}{4} \right) + \frac{1}{(2\pi^2 b)^{1/2}} \left\{ \cos a \int_0^{\left(\frac{b}{2}\right)^{1/2} k_0} dy \cos y^2 \right. \\ &\quad \left. - \sin a \int_0^{\left(\frac{b}{2}\right)^{1/2} k_0} dy \sin y^2 \right\}. \quad (23) \end{aligned}$$

The integrals in this case are well known, and the result is valid over a large area of t . At $t=1$ second, (23) gives $\xi=0.134$, as against 0.135 as given in the table on page 186.

Fig. 2.



If we now take $x/\sqrt{gh}t=0.5$, we have $z_0=k_0h=1.522$, $a=-0.414\sqrt{\frac{g}{h}}t$, $b=0.266\sqrt{gh^3}t$, $c=-0.3\sqrt{gh^5}t$. The auxiliary phase curve given by (20) is a cubic, which agrees closely with the true phase curve near the point of stationary phase P, but differs from it in type beyond the point of inflexion A.

It is clear from the diagram of figure 2, in which OPQ represents the true phase curve, that no single curve can

replace the true phase curve over its full range. Over the finite range from $z=0$ to $z_0=1.522$, it is best to employ the true phase curve itself, though a fairly accurate result is obtained by replacing it by a sine curve, $a \sin \frac{\pi z}{2z_0}$. Thus, for this portion of the curve the integration along the true phase curve leads to the result $\xi_1 = \frac{.278}{2\pi}$ or $.044$. For the range from $z_0=1.522$, the stationary phase point, to $z=\infty$ we might employ the auxiliary phase curve $\phi = \left(a + \frac{b\sigma^2}{2}\right)$. This gives us

$$\xi_2 = \frac{1}{2\pi} \int_0^\infty d\sigma \cos \left(a + \frac{b}{2}\sigma^2\right), \quad \dots \quad (24)$$

and at $t=1$ the value obtained for ξ_2 is $+.062$, and with $\xi = \xi_1 + \xi_2$, ξ is $.106$. According to our former calculation ξ is $.15$, so that in this case the auxiliary curve employed does not give a sufficiently close approximation at $t=1$. The above auxiliary curve, represented in the diagram by the dotted line RPS, is moderately close to the true phase curve in the range from $z=0$ to $z=3$, or even 4, but, as the diagram shows, it is not in sufficiently good agreement with the true phase curve beyond $z=4$. Another approximate value is obtained if we employ this dotted curve in the range $z=0$ to $z=4$, thus giving

$$\xi_1 = \frac{1}{2\pi h} \int_{-z_c}^{4-z_0} dz \cos \left(a + \frac{b}{2h^2}z^2\right), \quad \dots \quad (25)$$

in which the origin of z is at the point of stationary phase P. In the range from $z=4$ to $z=\infty$ we may take

$$\xi_2 = \frac{1}{2\pi h} \int_4^\infty dz \cos \left[\sqrt{\frac{g}{h}} \cdot t (z\alpha - z^{1/2}) \right], \quad \dots \quad (26)$$

which is identical with the corresponding integral for the case of infinitely deep water, being obtained from (13) by putting $\tanh kh = \tanh z = 1$. By means of the substitution $y^2 = \sqrt{\frac{g}{h}} \cdot t\alpha \left(z^{1/2} - \frac{1}{2\alpha}\right)^2$, we can transform the expression (26) into

$$\begin{aligned} \xi_2 = & -\frac{1}{2\pi h} \frac{1}{\sqrt{\frac{g}{h}} \cdot t\alpha} \sin \left(\kappa^2 - \sqrt{\frac{g}{h}} \frac{t}{4\alpha} \right) \\ & + \frac{1}{2\pi h} \cdot \frac{2}{\left(\sqrt{\frac{g}{h}} t\alpha\right)^{1/2}} \cdot \int_\kappa^\infty dy \cos \left\{ y^2 - \sqrt{\frac{g}{h}} \frac{t}{4\alpha} \right\}, \quad (27) \end{aligned}$$

where $\kappa^2 = \sqrt{\frac{g}{h}} \cdot t\alpha \left(4^{1/2} - \frac{1}{2\alpha} \right)$. Corresponding to

$$\alpha = \frac{v}{\sqrt{gh} \cdot t} = \cdot 5, \quad h=2, \quad t=1,$$

we obtain $\xi_1 = \cdot 128$, $\xi_2 = \cdot 007$, and $\xi = \cdot 135$ instead of $\cdot 15$ as given by our former calculation. The discrepancy remaining in the results given by the two different methods is due to the fact that even in the range $z=0$ to $z=4$ the auxiliary phase curve indicated by the dotted line is not sufficiently close to the true phase curve; and the above calculations are given to indicate the limitations to the use of the method of stationary phase in certain cases. The auxiliary phase curve,

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 = a + \frac{b}{2h^2} (z - z_0)^2 + \frac{c}{6h^3} (z - z_0)^3,$$

is, as is to be expected, better than the dotted curve, being almost in exact agreement with the true phase curve over the range from $z=0$ to $z - z_0 = -\frac{b}{c}$, the point of inflexion on the auxiliary curve; that is, from $z=0$ to $z=2\cdot 412$ in the present case ($\alpha = \cdot 5$). For this range we have

$$\xi_1 = \frac{1}{2\pi h} \int_0^{z_0 - \frac{b}{c}} dz \cos \left\{ a + \frac{b}{2h^2} (z - z_0)^2 + \frac{c}{6h^3} (z - z_0)^3 \right\},$$

$$z_0 - \frac{b}{c} = 2\cdot 412, \quad . \quad . \quad . \quad . \quad (28)$$

as a very close approximation to the correct value of the integral. For the range from $z=2\cdot 412$, the best result obtainable by means of an auxiliary curve is given by

$$\xi_2 = \frac{1}{2\pi h} \int_{z_0 - \frac{b}{c}}^{\infty} dz \cos \left[\sqrt{\frac{g}{h}} \cdot t(z\alpha - z^{1/2}) \right]. \quad . \quad (29)$$

The auxiliary curve employed in this agrees closely with the true curve in the range $z > 4$, but gradually falls below it in the range from $z=4$ to $z=2\cdot 412$. The numerical results at $t=1$ are here $\xi_1 = \cdot 047$, $\xi_2 = \cdot 093$, and $\xi = \cdot 140$. By employing the true phase curve in the range from $z=2\cdot 412$ to $z=4$, the value obtained is $\xi = \cdot 143$, which is in fair agreement with the result given by the series in the table on page 186 namely, $\xi = \cdot 15$. As stated earlier, the value given by the series may, in this case, be inaccurate to four or five per cent.,

and, in addition, the second integral in (2) has still to be added to the value obtained above, as its value increases as α diminishes, and at $\alpha = .5$ it is no longer negligible.

When we proceed to values of $x/\sqrt{gh}.t$ less than .5, the point of stationary phase P moves further and further from the origin. For the portion of the true phase curve from z_0 to ∞ , the value of ξ_2 given by (29) approximates closer to the true value of the integral as z_0 increases. The portion of the true phase curve OP is represented very closely by the cubic (20) as far as $\alpha = .4$, which corresponds with the value $z_0 = 2$. But for $z_0 > 2$ the cubic tends to fall below the true phase curve, and it ceases to give a sufficiently close approximation to the value of the integral for the portion OP of the true phase curve. When $\alpha < .4$, $z_0 > 2$, the true phase curve OP lies between the curves $\phi = a \sin \frac{\pi z}{2 z_0}$, and $\phi = \sqrt{\frac{g}{h}}(z\alpha - z^{1/2})$,

for both of which the integrals can be evaluated. It agrees closely with the latter curve when z_0 is considerably larger than 4, and the whole phase curve then is nearly identical with the corresponding curve for infinitely deep water. A cubic auxiliary phase curve which is in fairly good agreement with the true phase curve over range OP can always be obtained by taking a and b to fit the true phase curve at P as formerly, and by then choosing c so that the auxiliary curve passes through the origin. This method requires the values of the integrals

$$\int_0^A dw \cos \frac{\pi}{2}(w^3 - mw) \quad \text{and} \quad \int_0^A dw \sin \frac{\pi}{2}(w^3 - mw)$$

for all values of m and A , and these can be obtained readily by means of results given in a former paper provided

$$\int_0^A dw \cos \frac{\pi}{2} w^3 \quad \text{and} \quad \int_0^A dw \sin \frac{\pi}{2} w^3$$

are first determined. But the work of preparing the numerical values required for the convenient application of the stationary phase method to the evaluation of any integral must meantime be reserved for a later paper.

In the present paper we have proved by means of the evaluations given above, corresponding to $t=1$, that the method of stationary phase can be applied to integrals of the type (13) without the restriction to large values of t contained in former applications. All the evaluations of ξ given above, corresponding to various values of α , are valid for all

values of t ; and it is possible, therefore, by this method to trace the development of the wave-system as time advances. The effect of an increase in t can be most readily determined by writing the phase ϕ in the form

$$\phi = [k\{x - Vt\}] = t \left\{ k \frac{dkV}{dk_0} - kV \right\}.$$

In this we are treating $\frac{x}{t}$ as a constant, corresponding to the α employed above, x being the point at which the phase is stationary for wave-length $2\pi/k_0$. When we express ϕ , the true phase, in a series of terms depending on σ or $(k - k_0)$, it now takes the form

$$\phi = t \left\{ \alpha_0 + \frac{\beta_0}{2!} \sigma^2 - \frac{\gamma_0}{3!} \sigma^3 + \text{etc.} \right\}$$

instead of

$$\phi = a + \frac{b}{2!} \sigma^2 + \frac{c}{3!} \sigma^3 + \text{etc.},$$

as given in my former paper*.

From this it appears that if we take the true phase curve and the corresponding auxiliary phase curve at $t=1$, we have to increase the ordinates of each of these curves in the same ratio ($t/1$) to obtain the true phase curve and auxiliary phase curve at any later time t . The fit of the curves giving the correct result and the approximate result respectively is not altered as t increases. This does not necessarily prove that the approximation to the true value of the integral obtained by means of the auxiliary curve is equally good for all values of t . A test would need to be made in each individual case to prove this. Thus, in the case where the true phase curve is given by $\phi = t\{\beta\sigma^2 + \gamma\sigma^3\}$ and the auxiliary phase curve is given by $\phi = t\{\beta\sigma^2\}$, it is easy to show that the integral

$$\int_0^\infty d\sigma \cos\{t(\beta\sigma^2 + \gamma\sigma^3)\}$$

is represented with fair accuracy by

$$\int_0^\infty d\sigma \cos\{t\beta\sigma^2\} \quad \text{when } t \text{ is large, and the accuracy of the}$$

approximate value improves as t becomes larger. We have, in fact, the approximate evaluation, for β and γ positive,

$$I = \int_0^\infty d\sigma \cos\{t(\beta\sigma^2 + \gamma\sigma^3)\} = \frac{1}{2} \sqrt{\frac{\pi}{2\beta t}} \left\{ 1 - \frac{5.3.1}{2^3.2!} \frac{\gamma^2}{\beta^3 t} \right\},$$

the approximate evaluation being given by the first term

* Phil. Mag. xlv. pp. 1156-1167, June 1923.

alone. The above example indicates the reason why t must be taken large in Lord Kelvin's original applications of the principle of stationary phase.

In the evaluations of the integral (13) we have confined our attention to the range of x and t for which the phase curve has a stationary point. At time $t=1$ a stationary point exists on the phase curve for all values of x from 0 to 8. From $x=8$ to $x=\infty$ the phase curve has no stationary point. It is then of the same type as the phase curve $\phi=kx+\sigma t$, which appears in the second integral in equation (2) and which we have treated as negligible throughout. The corresponding integrals represent a disturbance which diminishes rapidly towards zero as x increases, of the type indicated by the advanced portion of the curve shown in

Fig. 3.

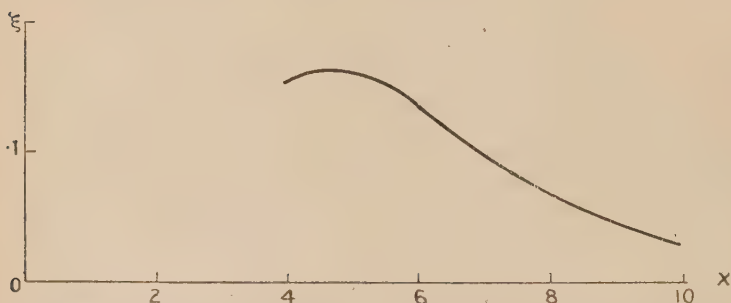


figure 3, which represents the displacement curve at $t=1$ in the range from $x=4$ to $x=10$ to which our calculations refer. These integrals can be evaluated by the method employed above, in which the true phase curve is replaced by an auxiliary curve, but for this evaluation the integrals referred to on page 194 above are again required.

The following table gives the numerical values from which the curves in figure 1 are obtained :—

z .	$F(z)$.	$-F''(z)$.	$-F'''(z)$.
0.0	1.000	.000	1.000
.25	.970	.234	.814
.5	.890	.388	.404
.75	.784	.439	.02
1.0	.676	.411	-.212
1.5	.506	.273	-.301
2.0	.398	.161	-.173
3.0	.296	.063	-.049
4.0	.250	.034	-.016

XVII. *Bending Stresses in Thin-Walled Tubes.*

By JOHN CASE, M.A., F.R.Ae.S.*

1. *Summary and Conclusions.*

THE object of the present paper is the investigation of the stresses in a thin tubular beam, such as steel factory chimneys, monocoque fuselages of aeroplanes, the hulls of submarine vessels, and the like. Beams such as these are liable to fail at a smaller load than is that calculated by the simple theory of bending, and, so far as the author is aware, no method of calculating the strength in these cases has been given before. The method developed here is perfectly general in principle, and can be applied to thin tubular beams of any cross-section, such as submarine hulls or steel spars for aeroplanes.

Considering, first, beams of circular cross-section, it is shown below that any section of the beam behaves as a ring under an external radial pressure which varies from point to point of the circumference. On account of this pressure a ring such as ABC (fig. 1), of unit axial length, is subjected to a maximum bending moment

$$m = \frac{M^2 r^3 t}{4EI^2},$$

where M is the bending moment applied to the beam, r is the mean radius of the cross-section, t is the thickness of the walls of the tube, I the moment of inertia of the cross-section, and E is Young's Modulus. This bending moment acts in the plane of the cross-section, and gives rise to a stress

$$\frac{3}{2} \frac{M^2 r^3}{EI^2 t} = \frac{3}{2} \frac{M^2}{\pi^2 E r^3 t^2}$$

at the points of the section which are in the principal plane of bending and points separated from these by 90° .

It will be seen that this stress, which is of opposite sign on the outer and inner surfaces of the tube, increases as the square of the applied couple, and inversely as the cube of the diameter and the square of the thickness of the cross-section.

It is shown below that this circumferential stress will exceed the longitudinal stress f if

$$\frac{r}{t} > \frac{E}{6f}.$$

* Communicated by the Author.

If we take f as the yield point of the material, and the maximum stress as the criterion of breakdown, this means that in the case of a steel having a yield point of 50,000 lb./in.², the circumferential stress will cause failure if the diameter of the tube is 800 times the thickness. If the maximum stress difference is the criterion, the circumferential stress will become important for a smaller diameter of tube, since at some points in the section it will give rise to a compressive stress at right angles to a longitudinal tensile stress and *vice versa*. Thus, if the diameter is 400 times the thickness, the bending moment which the tube can stand is reduced by 15 per cent.

These figures will show that the circumferential stresses only become important when the ratio thickness/diameter is very small; I am of opinion that in these cases it is the circumferential stresses which bring about the so-called buckling of the tube.

A similar expression to the above is given for an elliptic tube in equation (22) below, and the equations for any symmetrical section are given in (24) and (25). In the case of the hull of a submarine vessel, every cross-section is subjected to hydrostatic pressure as well as the pressure arising from flexure. If the hydrostatic pressure be written in the form $a - by$, where a and b are constants and y is the height of a point above the axis of the ship, which is here supposed to be of circular section, the circumferential stress is given by

$$\frac{3 M^2 r^3}{2 EI^2 t} \cos 2\theta + \frac{6br^3}{t^2} \left[\frac{2}{\pi} + \left(\frac{\theta}{\pi} - \frac{\pi}{4} \right) \cos \theta - \frac{\sin \theta}{2} \right],$$

where θ is measured from a horizontal diameter and the other letters have the same meaning as above.

Asymmetrical sections can be dealt with on the same principles as symmetrical sections, if due consideration is given to the distortion.

2. Beams of Circular Section (figs. 1 & 2).

Fig. 1.

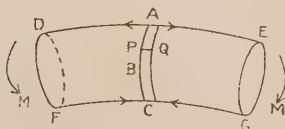
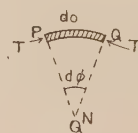


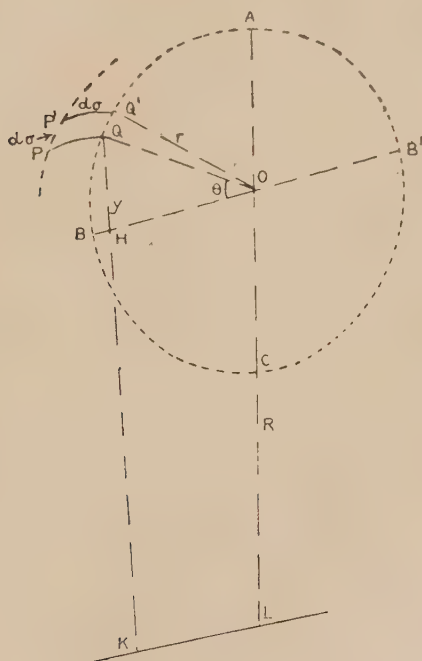
Fig. 2.



The beam is supposed under the action of couples M only.

The longitudinal fibres on the convex side DE are in tension and those on the concave side FG are in compression. Consider the ring ABC, and let PQ be an element of the top part of this ring, parallel to the plane of bending. This element will be acted on by forces of intensity T per unit area, exerted by the neighbouring rings, T being the stress intensity due to bending. Similar considerations will apply all round the ring. Thus, if we imagine the tube made up of a number of rings, each ring will be under the action of a radial pressure on account of the adjoining rings. This pressure will give rise to circumferential stresses in the ring.

Fig. 3.



We shall assume that each ring behaves as if it were entirely independent and acted upon by a radial pressure equivalent to the normal components of the stresses T .

In fig. 3, AOC is a diameter of one boundary of the ring, and lies in the plane of bending; BOB' is a diameter perpendicular to this.

KL is the intersection of the planes containing the boundaries of the ring, so that OL is the radius of the circle into which the centre line of the tube bends.

PP'Q'Q is an element of the ring, PQ and P'Q' being lines which before strain were parallel to the axis of the tube.

N is the intersection of the normals to the surface at P and Q (QON is a continuation of the radius QO).

Let $OL = R$,

$OQ = r$,

$QH = y$,

$PQ = d\sigma$,

$PP' = ds$,

$QK = \rho$,

$QKP = \phi$,

$QOH = \theta$,

T = tensile stress across PP' and QQ' ,

t = the thickness of the walls of the tube.

Then the total force on PP' and QQ' is $Tt \cdot ds$.

The radial pressure on the element due to these is

$$2Tt \, ds \frac{d\phi}{2} = Tt \, ds \cdot d\phi.$$

The area of $PP'Q'Q$ is $ds \cdot d\sigma$.

Hence the equivalent radial pressure on $PP'Q'Q$ is

$$p = \frac{Tt \cdot ds \cdot d\phi}{ds \cdot d\sigma} = Tt \frac{d\phi}{d\sigma} = \frac{Tt}{\rho} \quad \dots \quad (1)$$

Also

$$\rho = R + y = R + r \sin \theta \quad \dots \quad (2)$$

Assume that T is still given with sufficient accuracy by the usual formulæ, so that

$$T = \frac{My}{I} = \frac{Mr \sin \theta}{I} \quad \dots \quad (3)$$

where I is the moment of inertia of the section of the tube about BB' .

Hence, from (1), (2), and (3),

$$p = \frac{Mrt \sin \theta}{I(R + r \sin \theta)}, \quad \dots \quad (4)$$

but

$$\frac{1}{R} = \frac{M}{EI},$$

where E is Young's Modulus.

Hence

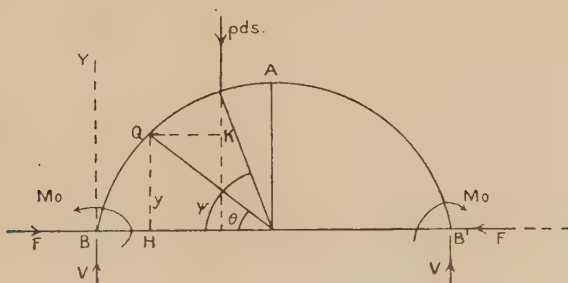
$$p = \frac{M^2rt}{EI^2} \cdot \frac{\sin \theta}{1 + \frac{r}{R} \sin \theta}.$$

Let us neglect r/R in comparison with unity, then

$$p = \frac{M^2rt}{EI^2} \sin \theta. \quad \dots \quad (5)$$

Consider, then, a ring of unit width subject to this radial pressure.

Fig. 4.



The action of the lower half on the upper can be represented by a bending moment M_0 , a tension V , and a shearing force F , as shown in fig. 4, at B and B'. Take B as origin, and measure x to the right.

By symmetry $F=0$.

Let m = bending moment at Q.

Then

$$\begin{aligned}
 m &= \int_Q^{B'} p ds \cdot QK - V \cdot HB' + M_0 \\
 &= \int_\theta^\pi p r^2 (\cos \theta - \cos \psi) d\psi - V r (1 + \cos \theta) + M_0 \\
 &= \frac{M^2 r^3 t}{EI^2} \int_\theta^\pi \sin \psi \cdot (\cos \theta - \cos \psi) d\psi - V r (1 + \cos \theta) + 0.
 \end{aligned}$$

Also,

$$\begin{aligned}
 V &= \int_0^{\frac{\pi}{2}} p \cdot r d\psi \\
 &= \frac{M^2 r^2 t}{EI^2} \int_0^{\frac{\pi}{2}} \sin \psi \cdot d\psi,
 \end{aligned}$$

which gives

$$V = \frac{M^2 r^2 t}{EI^2} \dots \dots \dots (7)$$

Substituting for (7) in (6) and evaluating the integral leads to

$$\begin{aligned}
 m &= M_0 - \frac{M^2 r^3 t}{4EI^2} (1 - \cos 2\theta) \\
 &= M - \frac{M^2 r^3 t}{2EI^2} \sin^2 \theta \dots \dots \dots (8)
 \end{aligned}$$

By symmetry the total change in the slope of the tangent to the ring between $\theta=0$ and $\theta=\frac{\pi}{2}$, due to deformation, must be zero. Therefore we must have

$$\begin{aligned}
 \int_0^{\frac{\pi}{2}} \frac{mr d\theta}{EI} &= 0, \\
 i. e. \quad \int_0^{\frac{\pi}{2}} \left(M_0 - \frac{M^2 r^3 t}{2EI^2} \sin^2 \theta \right) d\theta &= 0,
 \end{aligned}$$

since r , E , and I are constant, which gives

$$M_0 = \frac{M^2 r^3 t}{4EI^2}.$$

Hence, from (8),

$$m = \frac{M^2 r^3 t}{4EI^2} \cos 2\theta, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

m is a maximum when $\theta=0, \frac{\pi}{2}, \pi$, etc., and is zero when $\theta=\frac{\pi}{4}, \frac{3\pi}{4}$, etc.

The maximum value of m is $\frac{M^2 r^3 t}{4EI^2}$, which gives rise to a circumferential stress in the ring equal to $6m/t^2$, *i. e.*

$$\frac{3}{2} \frac{M^2 r^3}{EI^2 t} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

There is also the direct stress in the ring to be considered : the thrust at Q in the direction of the tangent is

$$\int_{\theta}^{\pi} pr \cos \theta d\psi - V \cos \theta,$$

which equals

$$\frac{M^2 r^2 t}{2EI^2} (1 + \cos 2\theta).$$

The corresponding stress is

$$\frac{M^2 r^2}{2EI^2} (1 + \cos 2\theta).$$

When $\theta=0$ or π , this = $\frac{M^2 r^2}{EI^2}$,

„ $\theta=\frac{\pi}{2}$, the direct stress = zero.

Hence the maximum stress in the ring, due to bending by the action of the radial force, is

$$\begin{aligned} & \frac{3}{2} \frac{M^2 r^3}{EI^2 t} + \frac{M^2 r^2}{EI^2} \\ &= \frac{3}{2} \frac{M^2 r^3}{EI^2 t} \left(1 + \frac{2}{3} \frac{t}{r}\right), \end{aligned}$$

which shows that we can neglect the direct stress.

Next we must consider the shearing force across the edge PQ (fig. 3). Denoting this by S , we see from fig. 4, that

$$S = \int_{\theta}^{\pi} pr \sin \psi d\psi - V \sin \theta.$$

Substituting for p from (5) and performing the integration, this leads to

$$S = \frac{1}{2} \frac{M^2 r^2 t}{EI^2} \sin 2\theta.$$

The cross-section of the ring is a rectangle of width unity and depth t , so that the shear stress is

$$q = \frac{3}{4} \frac{M^2 r^2}{EI^2} \sin 2\theta \quad . \quad . \quad . \quad . \quad (11)$$

at a point on the middle surface of the ring, being zero at the outer and inner surfaces.

The bending stress in the ring, due to the radial pressure, is a maximum on the outer and inner surfaces and zero on the middle surface. Also r/t will be large, so that, comparing (10) and (11), we see that we need not consider the shear stress.

Returning now to the element $PP'Q'Q$ of the tube, we see that there is a tensile stress

$$T = \frac{Mr \sin \theta}{I}$$

across the faces PP' and QQ' , and a tensile stress

$$T' = \pm \frac{3}{2} \frac{M^2 r^3}{EI^2 t} \cos 2\theta$$

along the outer and inner edges of the faces PQ and $P'Q'$.

When $\theta=0$ or π , T is zero, and T' is a tensile stress on the outer surface and a compressive stress on the inner surface.

When $\theta = \frac{\pi}{2}$ or $\frac{3\pi}{2}$,

$$T = \frac{Mr}{I} = \frac{M}{\pi r^2 t}, \quad . \quad . \quad . \quad . \quad (12)$$

$$T' = \frac{3}{2} \frac{M^2 r^3}{EI^2 t} = \frac{3}{2} \frac{M^2}{\pi^2 E r^3 t^3}, \quad . \quad . \quad . \quad (13)$$

the latter being compressive on the outer surface and tensile on the inner.

Let f be the yield stress of the material, then the bending moment which will cause the longitudinal stress to reach this value is given by

$$f = \frac{M}{\pi r^2 t},$$

$$i. e. \quad M = \pi r^2 t f.$$

The circumferential or hoop stress will then be (by 13)

$$\frac{\frac{3}{2}\pi^2 r^4 t^2 f^2}{\pi^2 E r^3 t^3},$$

which equals $\frac{\frac{3}{2}r}{t} \cdot \frac{f^2}{E}$. This will be greater than f if $\frac{\frac{3}{2}r}{tE} > 1$, i. e. if

$$\frac{r}{t} > \frac{E}{\frac{2}{3}f} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

In this case the tube will fail by hoop stress before it fails by longitudinal stress.

In the case of steel, if we take

$$E = 30 \times 10^6, \text{ and } f = 50,000 \text{ lb./in.}^2,$$

this means that the diameter of the tube must be about 800 times the thickness.

In the case of wood with

$$E = 1.5 \times 10^6 \text{ and } f = 5000 \text{ lb./in.}^2$$

the diameter must be about 400 times the thickness.

3. Submarine Hulls.

An extension of the above theory, which is applicable to submarine vessels of circular section, is when the tube is subjected to an external pressure which varies in a linear manner from top to bottom of the tube. In this case we can write:

$$\begin{aligned} p &= a - by + \frac{M^2 r t}{EI^2} \sin^2 \theta \\ &= a - br \sin \theta + \frac{M^2 r t}{EI^2} \sin^2 \theta, \quad \cdot \quad \cdot \quad \cdot \quad (15) \end{aligned}$$

where a and b are constants.

Proceeding in exactly the same way as before, we find

$$V = ar - \frac{\pi r^2 b}{4} + \frac{M^2 r^2 t}{EI^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (16)$$

$$M_0 = \frac{M^2 r^3 t}{4EI^2} - \frac{\pi^2 - 8}{4\pi} br^3, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (17)$$

$$m = \frac{M^2 r^3 t}{4EI^2} \cos 2\theta + br^3 \left[\frac{2}{\pi} + \left(\theta - \frac{\pi}{4} \right) \cos \theta - \frac{\sin \theta}{2} \right]. \quad (18)$$

PQ is an element of arc ds , and then we have

$$p = \frac{M^2 t}{EI^2} \cdot PG$$

$$V = \frac{M^2 t}{EI^2} \int_A^B PG \cdot ds, \quad \dots \dots \dots (22)$$

m = bending moment at R

$$= M_A - HA' \cdot V + \frac{M^2 t}{EI^2} \int_R^{A'} PG \cdot HG \cdot ds, \quad \dots \dots (23)$$

M_A is given by

$$\int_A^B m \, ds = 0,$$

i. e.

$$sM_A = \int_A^B V \cdot HA' \, ds - \frac{M^2 t}{EI^2} \int_A^B \int_R^B PG \cdot HG \cdot ds,$$

where s = the length of the arc AB.

Hence :

$$\begin{aligned} M_A &= \frac{M^2 t}{EI^2} \int_A^B \int_A^B (PG \cdot HA' - PG \cdot HG) \, ds \\ &= \frac{M^2 t}{EI^2} \int_A^B \int_A^B GA' \cdot PG \cdot ds \quad \dots \dots \dots (24) \end{aligned}$$

The integrals are evaluated by marking off equal intervals of arc along the circumference of the section, measuring GA' and PG , and then plotting the integrands against s .

It is hoped that the method has been sufficiently explained above to enable the reader to deal with any particular case, for the process is not necessarily limited to the symmetrical cases which we have taken. The process should be applicable to such sections as those used for the very thin metal spars of aeroplanes.

When the tube is subjected to shearing forces and direct tensions or thrusts, as well as bending moments, the circumferential stresses due to bending can be found as above, and then the maximum principal stress should be found.

XVIII. *Statistical Equilibrium in relation to the Photo-electric Effect, and its Application to the Determination of Absorption Coefficients.* By E. A. MILNE, Fellow of Trinity College and Assistant Director of the Solar Physics Observatory, Cambridge*.

§ 1. *Absorption Coefficients and Probabilities.*

ONE of the desiderata in the physics of the atom is a knowledge of the probability of transitions between different stationary states. Suppose we have an atom in a stationary state which we denote by 1, and that it can also assume another stationary state which we denote by 2. Let the probability that at any instant t the atom will in the succeeding interval dt undergo a transition from state 1 to state 2 be $P_{1 \rightarrow 2} dt$. Here $P_{1 \rightarrow 2}$ is a function of the circumstances of both the states 1 and 2, and also of the environment—that is to say, it may depend in addition on the chances of interference of the atom by another atom during the interval dt and also on the field of radiation to which the atom is subject. We will, however, exclude from consideration the former of these environmental conditions. If the state 1 is of less energy than the state 2, the transition will take place with absorption of radiant energy of a certain frequency ν .

If now the numerical value of $P_{1 \rightarrow 2}$ is known, we can find the absorption coefficient, for frequency ν , of the substance composed of these atoms. For the absorption coefficient is the product of two factors, one proportional to the number of atoms per unit mass capable of absorbing radiation of frequency ν , *i.e.* in the state 1, the other proportional to the probability that any given atom in the state 1 will in fact absorb. The first factor can be found, at least in many cases, from statistical mechanics, and thus the macroscopic absorption coefficient can be calculated if the probability of atomic transition is known.

Conversely, from the measured value of an absorption coefficient the probability of transition can be calculated. Now, in the X-ray region, where the process of absorption gives rise to continuous bands, the absolute values of absorption coefficients are known with accuracy. But in the optical region absorption is for the most part monochromatic, and here the measures are very difficult—hardly

* Communicated by the Director of the Solar Physics Observatory, Cambridge.

any, in fact, exist. Such a measure, for example, in the case of the D lines of sodium, would involve the exact determination of the ratio of the intensity inside the fine absorption line formed by interposing a known thickness of sodium vapour under known conditions in the path of a beam, to the intensity of the corresponding portion of the continuous spectrum of the beam itself.

Wood's measurements* of the absorption of mercury resonance radiation $\lambda 2537$ ($1S-2p_{1/2}$) in mercury vapour give values of the mass-absorption coefficient ranging from 0.8×10^9 to 2×10^9 ; for example, a layer of mercury vapour 0.5 mm. thick at 0.001 mm. pressure reduced the intensity of a beam of resonance radiation to $\frac{1}{3}$ of its initial value, a layer 2.5 mm. thick to $\frac{1}{16}$. In view of the values for ordinary X-rays (of the order of 10^0 to 10^2), and of Eddington's value for the material of the interior of a star (of the order of 20-40), such a value appears perhaps astonishingly large, though it is known that vapours are highly absorbent to radiations they themselves emit. Unfortunately, the writer has not been able to find any other experimental data on the subject. But it has been shown from rough considerations arising out of the assumed equilibrium of ionized calcium vapour under selective radiation pressure in the sun's chromosphere† that the mass-absorption coefficient for the H and K lines of calcium should be at least of the order of 10^8 , and probably somewhat greater.

In a similar way, if $P_{2 \rightarrow 1} dt$ is the probability of transition from state 2 to state 1 which occurs with emission of ν -radiation, then $P_{2 \rightarrow 1}$ is connected with the coefficient of emission. It is also connected with the average time of occupancy of an outer orbit by a displaced electron, which is usually denoted by τ . An electron ejected to an outer orbit appears to have a natural tendency to return to the normal orbit, and the average time of existence of the atom in the excited condition has been made the subject of experiment. It appears that τ is of the same order of magnitude, 10^{-8} sec., for the different lines of the different elements that have been investigated‡. Hence $P_{2 \rightarrow 1}$ is of the order of magnitude of 10^8 sec.⁻¹. But it must be noted that the probability $P_{2 \rightarrow 1}$ must be supposed in general to be the sum of two terms, one depending on the intensity of the surrounding radiation, the other depending on the inherent tendency of the electron to return to the state 1.

* Quoted by Foote and Mohler, 'The Origin of Spectra,' p. 89 (1922).

† Fowler and Milne, 'Monthly Notices,' lxxxiii. p. 418 (1923).

‡ Foote and Mohler, *loc. cit.* p. 96.

Bohr's correspondence principle connects the probabilities of transitions between stationary states with the magnitudes of the amplitudes of the corresponding harmonic components in the trigonometrical series which represents the motion. As is well known, it has predicted results of prime importance concerning the relative intensities, for example, in the components of the Stark effect and in the theory of fine structure, but it has not yet provided information as to the absolute values of the probabilities of transitions.

It is, however, the absolute values of the absorption coefficients, and thus of probabilities, that are required in many cases, in particular in the astrophysical investigations out of which the present paper originated. When an absorption line reaches its maximum intensity in the stellar sequence of spectra, it appears to originate in the stellar atmosphere at a depth where the pressure is of the order of 10^{-4} atmos., and the question arises how this may be accounted for on *a priori* grounds. When a detailed theory is constructed, on whatever specific assumptions, the mean pressure for a maximum of intensity in an absorption line is found to depend on the absolute value of the absorption coefficient. In fact, without a detailed calculation, it is clear that the greater the absorbing power of the atoms in question the more opaque is the stellar atmosphere in the frequency concerned, and so the greater the height and the smaller the pressure at which the line originates. From the observed pressure, it is possible on certain assumptions to obtain a relation between the absorption coefficient and certain physical characteristics of the star itself, such as the value of gravity at the surface. Assuming values for the latter, it is possible to obtain estimates of the absolute values of the absorption coefficients of certain spectral lines based entirely on astronomical evidence. Such estimates are in no serious disagreement as regards order of magnitude with the observational value for the Hg line and the value for the H and K lines of Ca deduced by a different line of astrophysical argument. But the estimates are subject to large uncertainties, and it is highly desirable to have them confirmed in any ways that are available.

§ 2. Einstein's Method.

The introduction of probability coefficients such as $P_{1 \rightarrow 2}$ and $P_{2 \rightarrow 1}$ was first made by Einstein* in a classical paper.

* *Verh. d. D. Phys. Gesell.* 1916, p. 318. A more detailed treatment is given in *Phys. Zeit.* xviii. p. 121 (1917).

Einstein considered an enclosure containing a gas whose atoms could assume a number of stationary states, and investigated the equilibrium subsisting between the atoms and the surrounding radiation. He assumed that the transitions between the stationary states were governed by certain definite laws of probability of the kind outlined in § 1 above. Each transition is accompanied by an emission or absorption of radiation, and the totality of transitions must give rise to black body radiation in the enclosure. From this, utilizing the statistical distribution of the atoms amongst the different stationary states, he deduced three results: (1) the quantum formula $h\nu = \Delta W$, for the connexion between frequency and energy change; (2) Planck's formula; (3) a relation equivalent in our notation to one between $P_{1 \rightarrow 2}$ and $P_{2 \rightarrow 1}$. Since the order of magnitude of $P_{2 \rightarrow 1}$ is known from the experimental determination of τ , and since $P_{1 \rightarrow 2}$ determines the coefficient of absorption, the possibility suggests itself of utilizing Einstein's relation to deduce the latter from the former.

The details are given in § 5. It will be found that unfortunately the relation does not yield at present a definite numerical value for $P_{1 \rightarrow 2}$, owing to a fresh unknown quantity which discloses itself, namely, the numerical width of a "monochromatic line."

§ 3. *Scope of the present Paper.*

In an attempt to avoid this difficulty, the author has in § 8 applied Einstein's method to the photo-electric liberation of electrons in a gas at a high temperature, with the production of ionization. An investigation is given of the thermodynamic equilibrium subsisting between atoms, ions, electrons, and radiation in an enclosure at a given temperature*. Just as Einstein's work evaluates the monochromatic absorption coefficients of the various lines of an

* Since this investigation was completed, a paper has appeared by Kramers (Phil. Mag. xlv. p. 836, Nov. 1923) in which Einstein's method is applied to the same problem. Kramers obtains a formula identical with (20) below, though the details of the deduction are different. Kramers' applications are to the absorption and emission of X-rays, *i. e.* to the inner levels of the atom, whilst the applications of the present paper are to the outer (optical) levels. Space does not permit a detailed comparison. Just as the present paper was being sent to the press, yet another paper on the same subject came to hand, by Becker (*Zeit. für Phys.* xviii. p. 325, 1923). This contains an investigation substantially equivalent to §§ 8-11 of the present paper.

optical series, so the extension to the photo-electric effect evaluates the coefficients of absorption for the continuous spectrum which lies on the short wave-length side of the series limit. Instead of the unknown theoretical breadth of a spectral line, it involves the unknown probability of capture of an electron by an ionized atom. By making definite assumptions about the probability of capture, the coefficient of absorption is evaluated. The result applies in the first instance to the optical region of frequencies. But for a heavily ionized gas at a high temperature this is precisely Eddington's problem of electron-capture in the interior of a star. The formula we obtain can, in fact, be integrated with regard to frequency, so as to give the mean coefficient of absorption of stellar material. The resulting formula agrees with Eddington's, save for a correcting factor which depends on the ionization potentials principally concerned.

§ 4. *General Remarks on Einstein's Method.*

When a case of dissociative equilibrium or any kind of statistical equilibrium is discussed with the aid of a specific kinetic theory, there appears an "equilibrium constant," a function (for any given system) of the temperature only, in the form of a ratio of reaction-velocities. When the equilibrium of the same system is discussed with the aid of thermodynamics, or from probability considerations, the same equilibrium constant appears, but its expression includes no reference to reaction-velocities, for the concept of reaction-velocities is foreign to pure thermodynamics. By confronting the two results, we obtain in general an explicit relation between the reaction-velocities. From thermodynamics alone the reaction-velocities can never be separately determined, but the form of the equilibrium constant imposes a restriction to which all detailed theories of the mechanism of the reactions must conform.

This is the point of Einstein's method. The thermodynamic theory of radiation (Kirchhoff) shows that if ϵ_ν is the coefficient of emission for frequency ν , k_ν the coefficient of absorption, then under equilibrium conditions $\epsilon_\nu/k_\nu = I_\nu$, where I_ν , the intensity of radiation, is a function of temperature only. Einstein's assumptions respecting stationary states and the probabilities of emission and absorption amounted to a detailed theory giving ϵ_ν and k_ν , and his results then followed from the condition $\epsilon_\nu/k_\nu = \text{function of temperature}$, combined with the thermodynamic properties of radiation. The probabilities of emission and absorption

may be regarded as the reaction-velocities of the monomolecular reaction consisting of the transition from one stationary state to another.

It is well known that early attempts at discovering the radiation formula were founded on this method applied in the reverse manner: I_ν was to be found by calculating ϵ_ν and k_ν from some particular atomic model. But familiarity with this instance perhaps obscures the fact that the method is capable of other applications.

The thermodynamic formula first freely used by Saha* for calculating the ionization of a gas at high temperatures is independent of the mechanism of ionization, but it imposes a restriction on any assumed mechanism of ionization and recombination. The mechanism of ionization assumed in § 8 is the photo-electric liberation of electrons; and a relation is found between the probability of ionization of a given atom by radiation and the probability of capture of an electron in a given type of encounter with an ion. But the existence of the thermodynamic state of equilibrium is in no way incompatible with other mechanisms of ionization. Thus ionization may occur by collisions between atoms. This process gives a rate of ionization proportional to the square of the pressure. If the only compensating process were that of the encounter of an ion with an electron, the rate of recombination would be also proportional to the square of the pressure, and therefore the equilibrium constant would be independent of the pressure, in disagreement with the thermodynamic formula and with observation. This shows that there must be some process of recombination other than that of the simple encounter of an ion and an electron. A principle of reversibility† shows that the true compensating process in the case of ionization by collision consists of *three-body encounters* between an ion, an electron, and another atom. The number of such encounters is proportional to the cube of the pressure; hence the ratio of the rates of recombination and ionization is proportional to the pressure simply, just as for ionization by radiation, in agreement with the thermodynamic formula‡.

Considerations of this kind would appear to have an important bearing on some of the vexed questions connected with the theory of monomolecular reactions.

* Phil. Mag. xl. p. 472 (1920).

† Cf. Klein and Rosseland, *Zeit. für Phys.* iv. p. 46 (1921).

‡ The ideas in this paragraph occurred independently and simultaneously to Mr. R. H. Fowler and the writer. See Mr. Fowler's paper on three-body encounters communicated to this Magazine.

§ 5. Application of Einstein's Formula to the Calculation of Monochromatic Absorption Coefficients.

Einstein's argument is as follows. Let 1 and 2 denote two definite stationary states of an atom, and let χ_1 and χ_2 ($\chi_1 > \chi_2$) denote their negative energies. Then the atom will proceed from the state 1 to the state 2 with absorption of radiation of amount $\chi_1 - \chi_2$, and from state 2 to state 1 with emission of the same amount. We assume this radiation to be monochromatic, of frequency ν . Let $A_{2 \rightarrow 1} dt$ be the probability that during the short time dt an atom in the state 2 will of its own accord change to the state 1, with emission of radiation. Einstein calls this "in-radiation." Again, let $B_{2 \rightarrow 1} I_\nu dt$ be the *additional* probability that the same atom will change to the state 1 in time dt under the influence of external isotropic radiation of intensity I_ν . Einstein calls this "out-radiation." Finally, let $B_{1 \rightarrow 2} I_\nu dt$ be the probability that an atom in the state 1 will change to the state 2 with absorption of radiation. The coefficients $A_{2 \rightarrow 1}$, $B_{2 \rightarrow 1}$, $B_{1 \rightarrow 2}$ depend only on the atomic states 1 and 2; in particular, they are independent of the temperature.

The relative numbers of atoms in the state 1 and 2, from statistical mechanics, are q_1 and $q_2 e^{-(\chi_1 - \chi_2)/kT}$, where T is the temperature, k is Boltzmann's constant, and q_1, q_2 are the weights of the states 1 and 2. As regards order of magnitude, q_1 and q_2 may be taken to be unity.

In equilibrium, the number of atoms which change from state 1 to state 2 during a time dt must be equal to the number which change from state 2 to state 1. The former number is proportional to

$$q_1 B_{1 \rightarrow 2} I_\nu dt,$$

the latter number to

$$q_2 e^{-(\chi_1 - \chi_2)/kT} (A_{2 \rightarrow 1} + B_{2 \rightarrow 1} I_\nu) dt.$$

Equating these and solving for I_ν , we find

$$I_\nu = \frac{A_{2 \rightarrow 1}}{(q_1/q_2) B_{1 \rightarrow 2} e^{(\chi_1 - \chi_2)/kT} - B_{2 \rightarrow 1}}.$$

This must be the intensity of black radiation of frequency ν at temperature T . When $T \rightarrow \infty$ we must have $I_\nu \rightarrow \infty$, and hence

$$q_1 B_{1 \rightarrow 2} = q_2 B_{2 \rightarrow 1}.$$

This gives

$$I_\nu = \frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \cdot \frac{1}{e^{(\chi_1 - \chi_2)/kT} - 1}.$$

Applying Wien's law, I_ν must be of the form $\nu^3 f(\nu/T)$. Hence $\chi_1 - \chi_2$ must be proportional to ν , which is Bohr's relation. Further,

$$\frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \propto \nu^3. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We thus arrive at Planck's formula. It is to be noted that had Einstein not assumed the occurrence of out-radiation, he would have arrived merely at the Wien approximation.

Now $A_{2 \rightarrow 1}$ is equal to $1/\tau$, where τ is as before the mean time of excitation of an atom in the state 2 when left to itself, and $B_{1 \rightarrow 2}$ determines the absorption coefficient. Our object is to endeavour to utilize (1) to calculate k_ν .

Einstein, however, in this deduction took no account of the fact that the ν -constituent of black radiation is not homogeneous radiation of intensity ν , but is an element $I_\nu d\nu$ of a continuous spectrum. Thus, if we wish to obtain the numerical form of (1), we must write in our probability definitions $B_{1 \rightarrow 2} I_\nu d\nu dt$, $B_{2 \rightarrow 1} I_\nu d\nu dt$, and we obtain then

$$I_\nu d\nu = \frac{q_2}{q_1} \cdot \frac{A_{2 \rightarrow 1}}{B_{1 \rightarrow 2}} \cdot \frac{1}{e^{h\nu/kT} - 1}.$$

Comparing this with the known value

$$I_\nu d\nu = \frac{2h\nu^3}{c^2} \cdot \frac{d\nu}{e^{h\nu/kT} - 1},$$

we find

$$\frac{B_{1 \rightarrow 2}}{A_{2 \rightarrow 1}} = \frac{q_2}{q_1} \cdot \frac{c^2}{2h\nu^3 d\nu} \cdot . \quad . \quad . \quad . \quad . \quad (2)$$

The magnitude of $d\nu$ is, however, undetermined. It is connected with the amount of the lack of sharpness of fixation of stationary states, which according to Bohr* should be comparable with the radiation during a complete orbital revolution calculated on classical principles. The same method† has, however, been used to calculate the entirely different magnitude τ , by assuming that τ is comparable with the time taken on the classical theory to emit the energy $h\nu$. The proper application of the correspondence principle would appear to be in doubt, though possibly both applications may be right.

* *Zeit. für Phys.* xiii. p. 151 (1923).

† See Foote and Mohler, *loc. cit.* p. 96.

§ 6. Numerical Values.

The connexion between $B_{1\rightarrow 2}$ and the mass absorption coefficient is obtained as follows. Suppose there are N atoms of the kind considered per unit volume, and that on the average the fraction f_1 of these are in the 1-quantum state. Then of the radiation $I_\nu d\nu \cos \theta d\omega dS dt$ incident in time dt , at an angle θ , within a pencil $d\omega$ on a small element of surface area dS and thickness dx , the fraction $k_\nu \rho dx \sec \theta$ will be absorbed, ρ being the density of the atoms considered. In terms of $B_{1\rightarrow 2}$, the amount absorbed is

$$Nf_1 dx dS \times B_{1\rightarrow 2} I_\nu d\nu dt \times \frac{d\omega}{4\pi} \times h\nu.$$

Equating the two amounts, we find

$$k_\nu = \frac{B_{1\rightarrow 2} h\nu f_1 N}{4\pi \rho}.$$

But $\rho/N = m'$, the mass of an atom. Hence

$$k_\nu = \frac{B_{1\rightarrow 2} h\nu f_1}{4\pi m'} \quad \dots \quad (2a)$$

Taking the estimate $k_\nu = 10^9$ for the Hg line $\lambda 2537$ ($1S - 2p_2$), for which $f_1 = 1$, $m' = 200 \times 1.64 \times 10^{-24}$, we find

$$B_{1\rightarrow 2} = 0.53. \quad \dots \quad (3)$$

Again, taking the chromospheric estimate $k_\nu = 10^8$ (a lower limit) for the Ca line $\lambda 3933$ ($1s - 1\pi_1$), for which $f_1 = 1$, $m' = 40 \times 1.64 \times 10^{-24}$, we find

$$B_{1\rightarrow 2} = 0.017 \text{ (lower limit)}. \quad \dots \quad (4)$$

For the sake of seeing the order of magnitude given by (2), let us take $\tau = 2 \times 10^{-8}$, whence $A_{2\rightarrow 1} = 0.5 \times 10^8$, and take $d\nu$ to correspond to a range 0.01 A.U. For definiteness take ν to correspond to $\lambda 3000$. Take also $q_1 = q_2 = 1$. We have then $d\nu = 3.3 \times 10^9$; whence from (2)

$$B_{1\rightarrow 2} = 1.0. \quad \dots \quad (5)$$

This is in agreement with (3) as regards order of magnitude, and therefore, in spite of the arbitrariness of our choice of $d\nu$, it must be regarded as confirming the large absolute values of the optical absorption coefficients. Arguments from the correspondence principle indicate smaller values of $d\nu$ than we have assumed, and

thus even larger absorption coefficients. But formula (2) will not be helpful in fixing the exact numerical values until precise definitions and determinations of dv are available.

§ 7. *Continuous Absorption.*

Beyond the limit of any optical series which appears as absorption lines there is in general a region of continuous absorption, which begins fairly abruptly at or near the series limit and fades away towards the violet side*. It has been pointed out by many writers† that towards the head of the series the intensity of the discrete absorption lines passes continuously into the intensity in the region of continuous absorption; actual inspection of spectrograms is very convincing on the point. If therefore we can calculate the absorption coefficient for the latter, we may assume it to give the absorption coefficient for the lines towards the head of the series, and therefore presumably also the order of magnitude of the coefficient for the earlier lines.

In what follows we calculate the absorption coefficient on the assumption that absorption on the high-frequency side of the series limit can only occur through the ejection of photo-electrons; and, similarly, that emission in this region can only occur through the capture of free electrons. Bohr has suggested, however, that transitions may occur, during the encounter of an electron with an atom, from one hyperbolic orbit to another with the emission of radiation; any such transition being a possible one, since hyperbolic orbits are non-quantizable. From the reversibility required by thermodynamic equilibrium it then follows that transitions between hyperbolic orbits must also be possible with the *absorption* of radiation. It would be possible to analyse these transitions in the light of statistical equilibrium. But the formulæ we shall obtain are not vitiated by neglect of processes of this kind; our formulæ in any case give us the absorption coefficient arising from the ejection of photo-electrons. The total absorption coefficient may however, be considerably bigger if absorption by free-free transitions is possible.

* On this subject reference should be made to an interesting letter by Wright, 'Nature,' June 24th, 1920, p. 810.

† *E.g.*, Sommerfeld, 'Atomic Structure and Spectral Lines,' p. 448 (1923).

§ 8. *Statistical Analysis of the Photo-electric Liberation of Electrons.*

Let us consider a quantity of partially ionized gas in dissociative equilibrium in an enclosure at a given temperature. Let the ionization potential be χ . For simplicity we will assume in the first instance that the gas consists of atoms of a single kind, that each neutral atom is capable of only one stationary state (so that each atom either is ionized or has its outermost electron in the state corresponding to negative energy χ), and that the amount of second or higher-stage ionization is inappreciable. These restrictions will be removed later. The atoms will be slow-moving compared with the free electrons. To a sufficient degree of approximation we can ignore the velocity of an atom in comparison with that of an electron encountering it.

Let N be the number of atoms per unit volume, x the degree of ionization, P the pressure, T the temperature, k the gas-constant per molecule (Boltzmann's constant), h Planck's constant, m the mass of an electron. Let q be the "weight" of the stationary state. Then the degree of ionization is given by the thermodynamic or statistical formula *

$$\frac{x^2}{1-x^2} P = T^{5/2} e^{-\chi/RT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma}{q h^3} \quad \dots (6)$$

Here σ is the symmetry number of the neutral atom ; it is equal to the number of equivalent electrons capable of being removed in first-stage ionization.

Let $\psi(\nu) I_\nu d\nu dt$ be the probability that a neutral atom will in time dt , under the influence of isotropic ν -radiation of intensity $I_\nu d\nu$, become ionized by absorption of a quantum of energy $h\nu$. The velocity v of the ejected electron is given by Einstein's law of the photo-electric effect,

$$h\nu = \frac{1}{2}mv^2 + \chi \quad \dots (7)$$

Since $N(1-x)$ is the number of neutral atoms, the total number of ν -quanta absorbed in time dt is

$$N(1-x) \psi(\nu) I_\nu d\nu dt \quad \dots (8)$$

Consider now the encounter with an ionized atom. We wish to calculate the number of encounters, with ionized

* For its most general derivation, see R. H. Fowler, *Phil. Mag.* xlv. p. 21 (1923). In virtue of our assumption of only one stationary state, the partition function $b(T)$ reduces to q . For the introduction of the symmetry number σ , see Fowler and Milne, 'Monthly Notices R. A. S.' lxxxiii. p. 407 (1923).

atoms, of electrons having velocities between v and $v + dv$, where the velocity-range dv is connected with the frequency range $d\nu$ by the relation

$$h d\nu = mv dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

obtained by differentiation of (7).

The number of free electrons per unit volume is Nx . By a known formula from gas-theory, according to Maxwell's law, the number of electrons with velocities between v and $v + dv$ and with velocity-directions lying inside an elementary solid angle $d\omega$ is

$$Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv d\omega.$$

We fix attention on v -electrons whose paths before encounter are so situated as to pass a given atom at a distance lying between p and $p + dp$. The number of such electrons encountering the given atom in time dt whose velocity-directions lie within a given cone $d\omega$ is

$$Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv d\omega \times 2\pi p dp \times v dt,$$

and hence the total number in all directions is

$$8\pi^2 Nx \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^3 dv p dp dt.$$

The number of ionized atoms per unit volume is Nx , and hence the total number of $(v, v + dv; p, p + dp)$ encounters is

$$8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^3 dv p dp dt.$$

Now let $f(v, p)$ be the probability that a (v, p) encounter results in capture. Then the number of captures in time dt is

$$8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} F(v) v^3 dv dt, \quad . \quad (10)$$

where

$$F(v) = \int_0^{p_0} f(v, p) p dp,$$

p_0 being the effective radius of the atom for capture-encounters; i. e., p_0 is defined by the relation

$$f(v, p) = 0, \quad (p > p_0).$$

In general, p_0 will be a function of v . If we write

$$\int_0^{p_0} f(v, p) 2\pi p dp = \pi s^2,$$

$$F(v) = \frac{1}{2}s^2,$$

then s is in Eddington's terminology* the "effective target radius"; for if the atom offered an actual target of radius s , we should have

$$f(v, p) = 1, \quad (0 < p < s);$$

$$f(v, p) = 0, \quad (p > s).$$

In equilibrium the number of ionizations with emission of v -electrons must be equal to the number of recombinations with v -electrons†. Equating (8) and (10), we have

$$N(1-x)\psi(v)I_\nu d\nu dt$$

$$= 8\pi^2 N^2 x^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} F(v) v^3 dv dt. \quad (11)$$

Now the total pressure P is given by

$$P = N(1+x)kT.$$

Inserting this in (11) and using the relation (9) between dv and $d\nu$, we find that (11) gives an equation for x which will be identical with the dissociation formula (6), provided

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 F(v)}{qh^2 \psi(v)} e^{-(\frac{1}{2}mv^2 + \chi)/kT}$$

$$= \frac{8\pi^2 m^2 \sigma v^2 F(v)}{qh^2 \psi(v)} e^{-h\nu/kT}. \quad (12)$$

But I_ν must be the intensity of black radiation,

$$I_\nu = \frac{2h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1}. \quad (13)$$

Identifying these, we have

$$\psi(v) = \frac{4\pi^2 m^2 \sigma v^2 F(v)}{qc} \left(\frac{c}{h\nu}\right)^3 (1 - e^{-h\nu/kT}), \quad (14)$$

where it should be remembered that v is connected with ν by relation (7).

* 'Monthly Notices,' lxxxiii. p. 35 (1922); lxxxiii. p. 431 (1923).

† The argument here is entirely independent of the extent to which ionization occurs by collision. See § 15 below.

§ 9. *Necessity for assuming that Capture can be stimulated by Radiation.*

Our object being to determine $\psi(\nu)$, equation (14) should contain the answer to the problem. But it makes $\psi(\nu)$ depend on the temperature, whereas $\psi(\nu)$ was defined as an atomic property, strictly independent of statistical variables such as the temperature. Our hypotheses have therefore led to a contradiction. It was to avoid a contradiction of this kind that Einstein made his assumption of "out-radiation," and we can obtain a form for $\psi(\nu)$ strictly independent of temperature by introducing an analogous assumption. We are compelled to suppose that external radiation can stimulate the capture of an electron, and we therefore assume that *there is an additional probability $g(\nu, p) I_\nu$ that a (ν, p) encounter will result in capture with emission of ν -radiation, ν and ν being connected by relation (7)* Write then

$$\int_0^{p_0} g(\nu, p) p dp = G(\nu).$$

Carrying through the analysis as before, we find that equation (12) becomes replaced by

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 [F(\nu) + I_\nu G(\nu)] e^{-h\nu/kT}}{qh^2 \psi(\nu)} \dots (12')$$

Solving for I_ν , we find

$$I_\nu = \frac{8\pi^2 m^2 \sigma v^2 F(\nu)}{qh^2 \psi(\nu) e^{h\nu/kT} - 8\pi^2 m^2 \sigma v^2 G(\nu)} \dots (15)$$

This will be identical with (13), provided

$$\frac{F(\nu)}{G(\nu)} = \frac{2h\nu^3}{c^2} \dots (16)$$

and

$$\psi(\nu) = \frac{4\pi^2 m^2 \sigma v^2 F(\nu)}{qc} \left(\frac{c}{h\nu}\right)^3 \dots (17)$$

Formula (17) gives $\psi(\nu)$ independent of T , thus removing the contradiction.

The ratio of the number of stimulated captures to the number of unstimulated captures is

$$\frac{G(\nu) I_\nu}{F(\nu)} = \frac{1}{e^{h\nu/kT} - 1}.$$

For the region of the spectrum in the neighbourhood of λ_{\max} , $h\nu/kT$ is about 5; so that in this region, and *a fortiori* for all higher frequencies, the proportion of stimulated captures is negligible. For low frequencies the ratio approximates to $kT/h\nu$, and so the stimulated captures are the important ones. But, of course, frequencies lower than χ/h do not come into consideration.

It will be seen that if either the radiation formula (13) or the dissociation formula (6) is known, the present method affords a means of deducing one of these from the other.

§ 10. Extension to Atoms capable of a Number of Stationary States.

Let the numerals 1, 2, ... denote the possible stationary states of a given neutral atom, arranged in order of decreasing negative energy. Let $\chi^{(1)}$, $\chi^{(2)}$ denote the (negative) energies of the levels; $\chi^{(1)}$ is now the ionization potential. Let q_1, q_2, \dots be the "weights" of the corresponding states. Then the fraction f_r of neutral atoms which are in the state r is given by

$$f_r = \frac{q_r e^{-(\chi^{(1)} - \chi^{(r)})/kT}}{b(T)}, \dots \dots \dots (18)$$

where $b(T)$ is the partition function defined by

$$b(T) = q_1 + q_2 e^{-(\chi^{(1)} - \chi^{(2)})/kT} + q_3 e^{-(\chi^{(1)} - \chi^{(3)})/kT} + \dots$$

Also the degree of ionization is given by

$$\frac{x^2}{1-x^2} P = T^{5/2} e^{-\chi^{(1)}/kT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma}{h^3 b(T)}. \dots \dots (19)$$

When an ionized atom captures an electron, the electron may be bound in any one of the stationary states. To every such state there corresponds a series limit, which we will denote by $\nu^{(r)}$, given by $h\nu^{(r)} = \chi^{(r)}$. The binding of an electron in the r -state will result in the emission of radiation of frequency $\nu > \nu^{(r)}$. Similarly for absorption, the gas will be capable of giving a series of continuous absorption bands, one for each $\nu^{(r)}$.

We use $\psi^{(r)}(\nu)$, $F^{(r)}(\nu)$, $G^{(r)}(\nu)$ in our probability definitions. Equating the number of photo-electric ejections

from the r -state to the number of bindings into the r -state*, we find

$$f_r N (1-x) \psi^{(r)}(v) I_\nu dv dt \\ = 8\pi^2 N^2 x^2 \left(\frac{m}{2\pi k T} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} [F^{(r)}(v) + I_\nu G^{(r)}(v)] v^3 dv dt.$$

On using (18) and (19), the function $b(T)$ cancels out, and we find

$$\psi^{(r)}(v) = \frac{4\pi^2 m^2 \sigma v^2 F^{(r)}(v)}{q_r c} \left(\frac{c}{h\nu} \right)^3, \quad \dots \quad (20)$$

where v and ν are now connected by the relation

$$h\nu = \frac{1}{2}mv^2 + \chi^{(r)}.$$

The only effect of the generalization to a number of stationary states is seen by comparison of (17) and (20) to be the introduction of the appropriate weight q_r .

§ 11. *Extension to Multiple Ionization and to Mixtures.*

Let χ_1, χ_2, \dots be the successive ionization potentials, *i. e.* the potentials corresponding to the removal, in the order mentioned, of the 1st, 2nd, ... electrons. (χ_1 is identical with the $\chi^{(1)}$ of § 10.) Let P_e be the partial pressure of electrons. Let x_r be the fraction of atoms whose ionization potential is χ_r , *i. e.* which have already lost $(r-1)$ electrons. The dissociation formula is

$$\frac{x_{r+1}}{x_r} P_e = T^{5/2} e^{-\chi_r/kT} \frac{(2\pi m)^{3/2} k^{5/2} \sigma_r}{q_r h^3}, \quad \dots \quad (21)$$

σ_r being the symmetry number and q_r the weight of the $(r-1)$ -fold ionized atom. For equilibrium we must have

$$x_r N \psi_r(v) I_\nu dv dt \\ = 8\pi^2 x_{r+1} N N_e \left(\frac{m}{2\pi k T} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} [F_r(v) + I_\nu G_r(v)] v^3 dv dt,$$

where N_e , the number of free electrons per unit volume, is given by

$$P_e = N_e kT.$$

* The number of ejections from the r -state to another stationary state are balanced by the number of gains by the r -state from other stationary states, Einstein's investigation holding for these. If the two kinds of gains and losses did not balance separately, the pressure would be involved differently for the two kinds, and we should get a discrepancy on combining with the radiation and dissociation formulæ.

On eliminating x_{r+1}/x_r , we arrive at the relation *

$$\psi_r(v) = \frac{4\pi^2 m^2 \sigma_r v^2 F_r(v)}{q_r c} \cdot \left(\frac{c}{h\nu}\right)^3, \quad \dots \quad (22)$$

where

$$h\nu = \frac{1}{2}mv^2 + \chi_r.$$

In this formula $\psi_r(v)$ refers to the probability of absorption by the $(r-1)$ -fold ionized atom with loss of an electron, $F_r(v)$, to the probability of capture by the r -fold ionized atom.

It will be noticed that in deducing (22) we have not assumed that the free electrons were derived only from ionization of the atoms in question; there has been no need to know the value of P_e . It follows that (22) holds also for a mixture of different kinds of atoms, ionized to any extent. Indeed this must be so, since (22) expresses a property of the atom itself, ψ and F being atomic functions.

§ 12. The Probability of Electron Capture.

At the series limit the velocity of ejection of the photo-electron is zero. Hence we have

$$\psi_r(v_r) = \frac{4\pi^2 m^2 \sigma_r}{q_r c} \cdot \left(\frac{c}{h\nu_r}\right)^3 \lim_{v \rightarrow 0} v^2 F_r(v). \quad \dots \quad (23)$$

Inspection of spectrograms shows that at and near the limit the absorption has a perfectly definite value, not zero and of course not infinite. Hence, from (23), $v^2 F(v)$ must have a finite non-zero limit as $v \rightarrow 0$. This means that for small speeds the probability of capture must obey approximately a law of the type

$$F(v) = \frac{\text{const.}}{v^2}. \quad \dots \quad (24)$$

It has been suggested by Eddington† that an electron is captured when it actually “hits the nucleus”; and using the inverse square law of force and taking account of relativity mechanics, he has given the formula

$$\begin{aligned} F(v) &= \frac{1}{2}s^2 = \frac{Zb(d + \frac{1}{2}Zb)c^2}{v^2} \\ &= \mu/v^2, \quad \dots \quad (25) \end{aligned}$$

* We have for simplicity omitted the generalization arising from the possibility of the $(r-1)$ -fold ionized atom possessing a number of stationary states. It would be easy to take account of the corresponding weights if required.

† *Loc. cit.*

say, where Z is the atomic number, d is the radius of the nucleus, and b is a constant given by

$$b = e^2/mc^2 = 2.81 \times 10^{-13} \text{ cm.}$$

It will be seen that this is of the form (24).

The validity of the assumption that capture depends on colliding with the nucleus has been criticized, but Eddington has shown that formula (25) leads to a value for the mean coefficient of absorption for stellar material in the interior of a star which is in agreement with the value he has deduced from the observed masses and luminosities of the stars. We shall return to the stellar absorption coefficient in § 15, but in the meantime we shall tentatively adopt Eddington's formula (25) as a working specification for $F(v)$. In doing so we are not necessarily adopting a nuclear-collision hypothesis: we are simply assuming that the probability of capture is inversely proportional to the square of the velocity not merely for small speeds (which we have shown independently to be the case), but for all the speeds we desire to consider; and that further the constant of proportionality has the numerical value deduced by Eddington.

§ 13. *Numerical Applications. Test of the Inverse Square Law.*

We will first apply formula (20) with $F(v)$ given by (25) to the continuous spectrum lying beyond the Balmer limit in the hydrogen spectrum. The atoms absorbing the Balmer lines or the associated continuous spectrum are in the second quantum state, and for hydrogen we have $q_r = r(r+1)$, so that $q_2 = 6$. For simplicity take $\lambda = 3000 \text{ A.U.}$ (the limit of the Balmer series is $\lambda 3647$). In (25) we take $Z = 1$, and there is no need to evaluate v , since with the inverse square law the function $v^2 F(v)$ occurring in the formula for $\psi(v)$ is independent of v . We have $\sigma = 1$, $h = 6.55 \times 10^{-27}$, $c = 3 \times 10^{10}$, $m = 9.00 \cdot 10^{-28}$. For the "radius of the nucleus" we may conveniently adopt the "radius of the electron"

$$d = \frac{2}{3}e^2/mc^2 = 1.87 \times 10^{-13} \text{ cm.}$$

We find then

$$F(v) = \frac{0.83 \times 10^{-4}}{v^2},$$

whence

$$\psi^{(2)}(v) = 1.4 \times 10^{-3}. \quad . \quad . \quad . \quad . \quad (26)$$

The corresponding value of the mass absorption coefficient k_v

for a hypothetical mass of hydrogen all in the 2-quantum state is given by

$$k_{\nu} = \frac{\psi^{(2)}(\nu) h\nu}{4\pi m'} = 4.5 \times 10^8$$

(using $m' = 1.64 \times 10^{-24}$). This is of the order of magnitude of the observed monochromatic coefficient for mercury and the chromospheric coefficient for ionized calcium*.

For $Z=80$, (Hg), taking now $q=1$ for the weight, we find similarly for $\lambda 3000$

$$\psi(\nu) = 23.4,$$

and for $Z=20$, (Ca), we find

$$\psi(\nu) = 1.55.$$

These are considerably larger than the corresponding *monochromatic* probabilities calculated in § 6, results (3) and (4). Eddington's formula (25) makes μ practically proportional to Z^2 , and so gives an enormously increased chance of capture for elements of high atomic number. But it must be remembered that we are considering for the moment the capture of an electron into the optical levels of a neutral (or almost neutral) atom, and the screening due to the other electrons may in this case reduce the effective atomic number for capture purposes. The stellar absorption coefficient is perhaps better given by the formula deduced by Eddington for non-relativistic orbits, which makes μ proportional to Z simply. If we increase the value of $\psi(\nu)$ for hydrogen simply in the ratio of the atomic numbers and

* It may be mentioned here that in some unpublished investigations the author has deduced from the observed temperature of the stars in which the Balmer lines reach their maximum ($10,000^\circ$) that in these stars

$$\frac{B_{2 \rightarrow n} h\nu}{4\pi m'} \cdot \frac{\omega}{g} = 3.6 \times 10^2,$$

where g is the effective value of gravity at the surface of the star and ω is the proportion by mass of hydrogen in the layer in which the Balmer lines originate. For such stars we may take $g=2 \times 10^3$. We are entirely uncertain as to the proportion of hydrogen, but if for definiteness we take $\omega=10^{-2}$ (one per cent. by mass—a reasonable value) we find for the Balmer lines

$$k_{\nu} = \frac{B_{2 \rightarrow n} h\nu}{4\pi m'} = 0.7 \times 10^3.$$

This "astronomical value" of the monochromatic absorption coefficient is of the order of magnitude calculated in the text for the continuous spectrum.

multiply by 6 for the change of q , we find for Hg

$$\psi(\nu) = 0.68,$$

and for Ca

$$\psi(\nu) = 0.17.$$

These numbers are in general agreement with the estimates of the monochromatic probabilities.

Whatever the precise mode of dependence on atomic number—the data are quite insufficient to decide this point,—it is clear that the photo-electric absorption coefficients are very high, and that the calculation confirms the general order of magnitude of the monochromatic absorption coefficients. We have seen that $F(\nu)$ must be proportional to ν^{-2} for small values of ν ; we are now entitled to say that an inverse square capture-formula of Eddington's type simultaneously allows us to deduce optical coefficients, of the order of 10^9 , and the stellar absorption coefficient, of the order of 40. The apparent range of validity of this formula for $F(\nu)$ is the more striking when we reflect that in the interior of a star the electronic velocities are of the order of 1.6×10^9 cm.sec. $^{-1}$, (720 volts), corresponding to a temperature of 5.6×10^6 degrees, whilst for the hydrogen atom, with $\chi^{(2)} = 3.39$ volts, the velocity of the photo-electron for $\lambda 3000$ is 5.1×10^7 cm.sec. $^{-1}$; for the Balmer limit itself the velocity is, of course, zero. It is to be expected that for high speeds, $F(\nu)$ will vary more rapidly with ν than the inverse square; but a departure from the inverse square in this direction in the velocity range here considered would lead to still higher values for the deduced optical coefficients, or conversely, assuming the optical coefficients, to a much smaller value for the stellar coefficient than is observed.

Whether this discussion affords genuine evidence for the validity of the inverse square law for the probability of capture over a considerable range of velocities can hardly be said definitely, but the writer is inclined to believe that it does. The results at least justify our continuing tentatively to adopt the inverse square law.

§ 14. *Inferences from the Inverse Square Law.*

If the inverse square law holds, we have immediately

$$\psi(\nu) \propto \nu^{-3}, \quad k_\nu \propto \nu^{-2},$$

for the law of absorption in the region beyond the series limit. This could presumably be tested by actual experiment.

Such experiments would afford valuable evidence as to the validity of the inverse square law if they could be carried to sufficiently high frequencies.

It may be recalled that the law of absorption of X-rays by matter on the high-frequency side of a limit is $k_\nu \propto \lambda^3 \propto \nu^{-3}$, which differs from our law for the optical case. The two are however in no way analogous; it is apparent, in fact, that considerations of statistical equilibrium on the foregoing lines can of themselves give no information concerning X-ray absorption until the temperature is so high that the ordinary temperature radiation contains X-ray frequencies in appreciable amounts, in which case however (as in the interior of a star) there would be intense ionization, the outer electrons would be largely stripped off, and the X-ray levels would play the part of optical levels *. (See § 18.)

The thermodynamics of the interaction of X-rays and matter has been considered by L. de Broglie†, and employed in an attempt to deduce the law $k \propto \lambda^3$ for the absorption of X-rays. In one part of his paper he envisages strict thermodynamic equilibrium, and obtains a formula for the probability of capture in terms of the absorption coefficient; he uses however not the dissociation formula, but Richardson's thermionic formula for the density of free electrons in an enclosure. But in the later parts of his paper he balances a fraction of the energy absorbed in the continuous absorption band against the energy emitted in the line spectrum, thereby violating the details of strict thermodynamic equilibrium. Further, to obtain the absorption law $k \propto \lambda^3$ he finds it necessary to introduce certain additional arbitrary assumptions. It is true that the absorption of an X-ray frequency by a normal atom with ejection of an electron from an inner level is followed, and probably followed very rapidly, by a series of monochromatic emissions as the electrons in the outer levels fall in; but in thermodynamic equilibrium each event must be reversible. If the successive events are linked in an unalterable sequence, as is likely in this case, then we are bound to regard them as forming a single event capable of occurring in the reverse direction—a succession of discrete absorptions followed by an emission; and it is the numbers of forward and backward events that must be balanced. This assumes, as seems probable, that the principle of the separate balancing of reversible events in thermodynamic equilibrium, which we have already seen to be necessary in certain cases,

* The λ^3 law would require a capture-probability function varying as the inverse fourth power of the velocity for high velocities.

† *Journ. de Physique*, iii. p. 33 (1922).

can be given a wider generalization, and invoked in cases where direct arguments from pressures and temperatures as to the independent balancing are not available.

For the monochromatic absorption-probability we found in § 5, equation (2),

$$B_{1 \rightarrow n} = \frac{c^2}{2h\nu^3 d\nu} \cdot \frac{q_n}{q_1} A_{n \rightarrow 1}.$$

The value of $B_{1 \rightarrow n}$ near the head of the series should pass continuously into the value of $\psi(\nu)$ given by (20). It will be noted that ν^3 occurs in the denominator of both expressions. Hence for large quantum numbers we should expect

$$\frac{q_n A_{n \rightarrow 1}}{d\nu} = \text{constant},$$

since here we may certainly take $\nu^2 F(\nu)$ as constant.

Concerning $d\nu$, since $h\nu = \chi^{(1)} - \chi^{(n)}$ the breadth of the line will depend on the limits of fixation of both the stationary states 1 and n . But for large n the energy values of the successive stationary states are close together, and the classical radiation from them would be small; hence we may suppose that $d\nu$ arises almost entirely from the limits of the state 1. In that case $d\nu$ will be independent of n when n is large, and hence for large n we should have

$$q_n A_{n \rightarrow 1} = \text{constant}.$$

Since for hydrogen $q_n = n(n+1)$, this would give for large n

$$\tau = \frac{1}{A_{n \rightarrow 1}} \propto n^2.$$

The rate of radiation from an orbit on the classical theory is proportional to n^{-8} , so that the assumption that it is the latter principle which determines τ is inconsistent with the result we have obtained from consideration of the continuity of transition from the binding of external electrons to the falling-in of electrons from orbits of large quantum number. The case for this continuity seems unassailable, and therefore either τ is not determined from the classical radiation, or else the assumption we have introduced about $d\nu$ is untenable. We shall not pursue this matter further.

§ 15. The Rate of Ionization.

By definition of $\psi(\nu)$, the total number of photo-electric ionizations per atom per second, in equilibrium, is

$$\int_{\nu_1}^{\infty} \psi(\nu) I_{\nu} d\nu,$$

where ν_1 is the series limit for the initial state concerned. Inserting for $\psi(\nu)$ and assuming the inverse square law, this becomes

$$\frac{8\pi^2 m^2 \sigma \mu}{q h^2} \int_{\nu_1}^{\infty} \frac{d\nu}{e^{h\nu/kT} - 1},$$

and provided χ/kT is not too small, this may be written approximately

$$\frac{8\pi^2 m^2 \sigma \mu}{q h^3} kT e^{-\chi/kT}.$$

For hydrogen at $10,000^{\circ}$, the number of photo-electric ionizations per second of an atom in the 2-quantum state is found to be

$$0.84 \times 10^8,$$

where we have taken $\chi = 3.39$ volts, and $q = 6$. Of course, at this temperature comparatively few of the neutral atoms are in other than the normal state; the fraction in the 2-quantum state is in fact 2.2×10^{-5} . The foregoing result is therefore best stated in the form that once an atom has been excited into the 2-quantum state, its average life in that state, as limited by photo-electric ionization, is about 10^{-8} sec. Other agencies of destruction, besides its own intrinsic tendency to return to the normal state, will naturally shorten this.

§ 16.

The Mean Absorption Coefficient for Highly-ionized Material at High Temperatures, averaged through the Spectrum.

For the coming-away of the r th electron we have obtained the formula

$$\psi_r(\nu) = \frac{4\pi^2 m^2 \sigma_r v^2 F_r(\nu)}{q_r c} \left(\frac{c}{h\nu} \right)^3.$$

The fraction of atoms $(r-1)$ -fold ionized and therefore in a position to lose the r th electron is x_r . Hence the contribution to the total mass-absorption coefficient due to these atoms is

$$k_r(\nu) = \frac{h\nu}{4\pi m} x_r \psi_r(\nu). \quad \dots \quad (27)$$

This holds for $\nu > \nu_r$, where $h\nu_r = \chi_r$. For $\nu < \nu_r$ the x_r -atoms are transparent, save for line-absorption due to the different stationary states of the $(r-1)$ -fold ionized atom. We shall omit any such line-absorption from consideration. This is equivalent to regarding each atom as possessing only one stationary state for each degree of ionization, though presumably each ionized "kernel" possesses a series of "optical" levels. However, we are determining only the continuous absorption, and are regarding the absorption coefficient of the material as a whole as due to the superposition of regions of continuous absorption arising from the loss of photo-electrons.

Suppose, now, that the probability of capture is the same for all stages of ionization*, *i. e.* suppose $F_r(\nu)$ the same for all r . Then the absorption coefficient of the whole material for frequency ν is given by

$$k(\nu) = \sum k_r(\nu) = \frac{\pi m^2 v^2 F(\nu)}{m'} \left(\frac{c}{h\nu} \right)^2 \sum_{r=1}^{\infty} \frac{\sigma_{r,r}}{q_r} \quad (28)$$

the summation being extended to all r 's for which $\chi_r < h\nu$. Thus for large ν , atoms in almost all stages of ionization will contribute, but for small ν , only atoms in the earlier ones can do so. Atoms in the earlier stages of ionization are effective throughout the greater part of the spectrum, atoms in the later stages only through the region of high frequencies. For high frequencies, therefore, the absorption coefficient of the whole mass varies as ν^{-2} , but as the frequency decreases, the absorption coefficient changes less rapidly, owing to the dropping-out of the more highly-ionized atoms. It would be an easy matter to obtain the march of $k(\nu)$ in any particular case, given the ionization potentials and the pressure and temperature.

To find the mean absorption coefficient, we must integrate through the spectrum. The mean absorption coefficient for black radiation is

$$\bar{k} = \int_0^\infty k(\nu) I_\nu d\nu / \int_0^\infty I_\nu d\nu,$$

but in our case the contribution from atoms in any given stage of ionization must be integrated only through the

* With Eddington's nuclear-collision theory of capture, this assumption holds; for $F(\nu)$ then depends only on the atomic number.

range of spectrum in which they are effective. We have then

$$\bar{k}_r = \frac{\pi m^2 c^2 \sigma_r x_r}{m' q_r} \frac{\int_{\nu_r}^{\infty} v^2 F(v) (h\nu)^{-2} I_\nu d\nu}{\int_0^{\infty} I_\nu d\nu}.$$

Assuming the inverse square law, we put $v^2 F(v) = \mu$ and take it outside the sign of integration. Introducing Planck's formula for I_ν , we have

$$k_r = \frac{\pi m^2 c^2 \mu \sigma_r x_r}{m' k^2 T^2 q_r} \frac{\int_{y_r}^{\infty} \frac{y dy}{e^y - 1}}{\int_0^{\infty} \frac{y^3 dy}{e^y - 1}},$$

where

$$y = \frac{h\nu}{kT}, \quad y_r = \frac{h\nu_r}{kT} = \frac{\chi_r}{kT}.$$

The integral in the denominator has the value $\pi^4/15$. For that in the numerator put

$$\int_{y_r}^{\infty} \frac{y dy}{e^y - 1} = e^{-y_r} \xi(y_r).$$

It is readily found that for y small

$$\xi(y) \sim \frac{1}{6}\pi^2 + y(\frac{1}{6}\pi^2 - 1),$$

and that for y large

$$\xi(y) \sim 1 + y.$$

The error of the latter approximation is only 5 per cent. for y so small as 2.

We have now

$$\bar{k}_r = \frac{15m^2 c^2 \mu \sigma_r x_r}{\pi^3 m' k^2 T^2 q_r} e^{-y_r} \xi(y_r).$$

We can eliminate $\sigma_r x_r e^{-y_r}/q_r$ from this by means of the dissociation formula (21). We find then

$$\bar{k}_r = \frac{P_e}{(kT)^{9/2}} \cdot \frac{15c^2 \mu h^3}{2\pi^4 m'} \left(\frac{m}{2\pi}\right)^{1/2} x_{r+1} \xi(y_r), \quad (29)$$

a formula which shows how the part of the absorption coefficient due to the $(r-1)$ -fold ionized atoms depends on the number of r -fold ionized atoms available for the compensating process of capture.

Summing for the whole material, we have

$$\bar{k} = \frac{P}{(kT)^{9/2}} \cdot \frac{15c^2\mu h^3}{2\pi^4 m'} \left(\frac{m}{2\pi}\right)^{1/2} \sum_{r=1} x_{r+1} \xi(\chi_r/kT). \quad (30)$$

This is the complete expression for the mean absorption coefficient in terms of the pressure and temperature and the successive ionization potentials.

§ 17. *Comparison with Eddington's Formula for k .*

A theoretical calculation of \bar{k} was first given by Eddington*. His method, involving the consideration of "electron lives," is the same in principle as that used in this paper, though it does not have regard to the finer details of the statistical equilibrium. He throughout worked with mean values—the mean velocity of an electron at temperature T , the mean value of a quantum at temperature T —and thus took no account of the dependence on frequency. Again, he treated all the atoms as on the same footing as regards their encounters with electrons. The present method takes account of the various amounts of ionization and of the various regions of the spectrum to which the atoms of various degrees of ionization contribute, and it is through this that our factor involving ionization potentials arises. It will be interesting to compare the formulæ in detail.

If A is the atomic weight of the element considered, M the mean molecular weight of the ionized system, m_H the mass of a hydrogen atom (so that $m' = Am_H$), the ratio of the number of free electrons to the number of atoms is $(A/M) - 1$, and hence, if ρ is the density,

$$P_e = \left(\frac{A}{M} - 1\right) \frac{\rho kT}{Am_H}.$$

Hence

$$\bar{k} = \frac{15\mu c^2 h^3}{2\pi^4 Am_H^2} \left(\frac{m}{2\pi}\right)^{1/2} \left(\frac{1}{M} - \frac{1}{A}\right) \frac{\rho}{(kT)^{7/2}} \sum_{r=1} x_{r+1} \xi(\chi_r/kT). \quad (31)$$

Eddington's value in our notation is

$$\bar{k}_{\text{Edd.}} = \frac{2\pi\mu k}{Am_H^2 aucM} \cdot \frac{\rho}{T^{7/2}} \times 2.70.$$

Here a is such that aT^4 is the energy density of black radiation, and so

$$a = \frac{8\pi^5}{15} \cdot \frac{k^4}{h^3 c^3};$$

* 'Monthly Notices,' lxxxiii. p. 32 (1922).

and u is the harmonic mean velocity of an electron at 1° absolute, and so

$$u = (\pi k / 2m)^{1/2}.$$

We have then

$$\bar{k}_{\text{Edd.}} = \frac{15\mu c^2 h^3}{2\pi^4 m_H^2 A} \left(\frac{m}{2\pi}\right)^{1/2} \frac{1}{M} \cdot \frac{\rho}{(kT)^{7/2}} \times 2.70. \quad (32)$$

Eddington uses the value $\mu = Zbc^2(d + \frac{1}{2}Zb)$, derived on the nuclear-collision hypothesis, but for the purpose of comparison we have preferred to leave μ unformulated, assuming only the inverse square law for the probability of capture.

It is seen on comparison of (31) and (32) that our more detailed method confirms Eddington's formula completely*, save for his factor 2.70 replacing our summation factor. This arises in Eddington's treatment from the use of the mean quantum at temperature T , which is equal to $2.70 kT$, the numerical factor being found from the relation

$$\frac{h\bar{\nu}}{kT} = \int_0^\infty \frac{y^3 dy}{e^y - 1} \bigg/ \int_0^\infty \frac{y^2 dy}{e^y - 1} = 2.70.$$

The numerical value of our summation factor is considered in § 18.

It has been argued by Lindemann† that Eddington's method is vitiated by the fact that he took no account of the electrons liberated by collision, tracing all the free electrons present to the action of radiation; that vastly greater numbers would be liberated per second by collisions; and that hence the mean free path of an electron would be smaller and thus the calculated "effective target area" (the quantity πs^2 of § 8) much larger to give the same observed absorption coefficient. Eddington, whilst denying that the amount of energy available for setting electrons free permits a number of captures appreciably different from the number he has calculated, yet remarks‡ that he would be "glad of data which would enable an estimate to be made of the number of additional electrons set free by collisions, so as to take account of the necessary correction if appreciable."

The method and results of the present paper show that the validity of Eddington's procedure (when refined so as

* The ionization being large, Eddington specifically neglects $1/A$ in comparison with $1/M$.

† 'Observatory,' xlv. p. 384 (1922); 'Monthly Notices,' lxxxiii. p. 332 (1923).

‡ 'Monthly Notices,' lxxxiii. p. 436 (1923).

to take account of the absorption coefficient as a function of frequency) is entirely independent of the extent to which ionization by collision occurs. The number of electrons free at any one instant is determined purely by considerations of probability and thermodynamics; dissociation must proceed to such an extent that the entropy is a maximum, whatever the mechanism of dissociation. Electrons may be (and almost certainly are) liberated in enormous numbers by collisions*; but such collisions have no effect whatever on the number free at any one instant, when the gas is in thermodynamic equilibrium. In so far as free electrons are produced by photo-electric action with absorption of radiation, they will be recaptured, to exactly the same extent, with the emission of radiation; in so far as free electrons are produced by collision between two bodies (say between an atom and an electron), to exactly the same extent they will be recombined by radiationless three-body encounters (of the ion, the electron to be bound, and another electron). A form of equilibrium might be imagined to exist in which the two sets of processes did not separately balance; but it would not lead to the thermodynamic dissociation formula. The equilibrium would, in fact, involve the pressure through a factor of the form

$$\frac{a_2 P^2 + b_2 P^3}{a_1 P + b_1 P^2},$$

in which the ratio of a_2/a_1 to b_2/b_1 would depend on the relative efficiency of the two processes. This is incompatible with the deduction of thermodynamics; we must have therefore $a_2/a_1 = b_2/b_1$, and the processes balance separately. We have seen, indeed, that for strict thermodynamic equilibrium it is necessary to suppose that captures are to some extent stimulated by external radiation, more particularly that a capture with emission of radiation of frequency ν is rendered more probable by the presence of external radiation of frequency ν ; but this does not affect the independence of the mechanisms or the form of the final expression for the absorption coefficient.

§ 18. *The Ionization-Potential Correcting Factor.*

It is easy to see in a general way the order of magnitude of the factor

$$\Sigma = \sum_{r=1} x_{r+1} \xi(\chi_r/kT)$$

* See Mr. R. H. Fowler's paper in the next number of this Magazine, § 5.

and of the significant ionization-potentials. Were the temperature so high that all the atoms were practically ionized down to their nuclei, χ_r/kT would be small for all values of r , and the value of ξ would be $\pi^2/6$ in each case. We should then have, since $\sum_1 x_r = 1$,

$$\begin{aligned}\Sigma &= \frac{1}{6}\pi^2 \sum_{r=1} x_{r+1} = \frac{1}{6}\pi^2(1-x_1) \\ &= \frac{1}{6}\pi^2,\end{aligned}$$

for x_1 , the fraction remaining neutral, must be negligible. The value of $\pi^2/6$ is 1.645, which is therefore the factor replacing Eddington's factor 2.70 in this case. For example, we could find in this way the opacity of hydrogen at a temperature so high that it was practically a mass of protons. It might be expected that under such circumstances the gas would be practically transparent, but the value comes out of the same order of magnitude as the stellar absorption coefficient for the same density and temperature. Comparatively few of the nuclei at any one instant possess an electron with which to absorb, but each one that does so possesses in effect the large-valued optical absorption coefficient.

When the temperature is not so high as this, a fair approximation for Σ is

$$\Sigma = \sum_{r=1} x_{r+1} \left(1 + \frac{\chi_r}{kT}\right).$$

This does injustice to the early x 's; for them, χ/kT is small and so the approximation gives the coefficient unity instead of $\pi^2/6$. However, these x 's are themselves very small, and the resulting error will not be serious. Again neglecting x_1 , we have then

$$\Sigma = 1 + \sum_{r=1} \frac{x_{r+1}\chi_r}{kT} = 1 + \frac{\bar{\chi}}{kT},$$

say, where $\bar{\chi}$ is the mean effective ionization potential. Since this will in general increase roughly proportionally to T (apart from complications arising from the factor $P/T^{5/2}$ in the dissociation formula), the value of Σ will be fairly steady. One after another, the successive stages of ionization will be dominant and control the value of $\bar{\chi}$.

The ratio of the fraction of r -fold ionized atoms to that of $(r-1)$ -fold ionized atoms is given by equation (21), and it is clear that $x_r > x_{r-1}$ so long as

$$\frac{0.332 \sigma_r T^{5/2} e^{-\chi_r/kT}}{q_r P_e} > 1.$$

(We have substituted for $(2\pi m)^{3/2} k^{5/2} h^{-3}$ its numerical value.) As r increases, χ_r increases, and the left-hand side of the inequality decreases. The stage of ionization most abundantly represented is thus the r' -fold stage, where r' is the greatest value of r for which

$$\frac{\chi_r}{kT} < \log \frac{0.332 \sigma_r T^{5/2}}{q_r P_e} \dots \dots \dots (33)$$

Contributions to $\Sigma x_{r+1} \chi_r$ will arise principally from values of r in the neighbourhood of this value.

As an example, take the typical stellar conditions used by Eddington :

$$T = 5.64 \times 10^6 \text{ degrees, } \rho = 0.0678 \text{ grm.cm.}^{-3}, \quad M = 2.83,$$

which give

$$P = 1.123 \times 10^{13} \text{ dynes.cm.}^{-2}$$

We may take this as giving also P_e . We then find that the relative abundance of the successive stages of ionization will increase so long as

$$\frac{\chi_r}{kT} < 2.3026 \log_{10} \frac{0.332 \times (5.64)^{5/2} \times 10^{15}}{1.123 \times 10^{13}} = 7.70.$$

For this temperature kT is 485 volts, and so the critical ionization potential is $485 \times 7.70 = 3730$ volts. If the atom in question possesses an ionization potential of this order we may adopt it for χ , and we have then

$$\Sigma = 1 + 7.70 = 8.70.$$

If, however, the atom does not possess an ionization potential of this order, we must take the next lowest one, and $\bar{\chi}/kT$ will be somewhat lower. For example, let us suppose that the r -fold stage is the most abundant, and that χ_r differs considerably from the two neighbouring potentials χ_{r+1} and χ_{r-1} . It is then easily seen that x_{r-1} and x_{r+2} may be neglected in comparison with x_r and x_{r+1} , and *a fortiori* the fractions of less and more ionized atoms respectively. Hence $\bar{\chi}$ reduces effectively to

$$x_r \chi_{r-1} + x_{r+1} \chi_r.$$

But now the fractions x_r and x_{r+1} comprise practically the whole number of atoms, and so $x_r + x_{r+1} = 1$. Hence

$$\bar{\chi} = \chi_{r-1} + x_{r+1}(\chi_r - \chi_{r-1}).$$

But $x_{r+1} \geq x_r$, and hence $1 \geq x_{r+1} \geq \frac{1}{2}$. Hence χ must lie between χ_r and $\frac{1}{2}(\chi_r + \chi_{r-1})$.

For iron* the L absorption limit is about 720 volts, the K-limit about 7100 volts. The ionization potentials for the removal of the corresponding L- or K- electrons after all the more loosely bound electrons have been detached will be considerably higher than these, but they will probably lie well on either side of the critical potential found above. Thus the iron atoms will be practically completely ionized as to their L-ring, but will mostly retain their K-ring †. The value of the correcting factor will be about $1 + 900/485 = 2.8$. On the other hand, for an element with an atomic number in the neighbourhood of 40 (Zr), the L-limit is about 2300 volts, the K-limit about 18,000 volts, and the value of the correcting factor would be about $1 + 2500/485 = 6.1$. In general it appears probable that a factor somewhat larger than Eddington's 2.70 will be required, though it will vary irregularly from place to place in the star.

Roughly speaking, the more nearly an element possesses an ionization potential approximating to the critical potential given by (33), the greater the absorption coefficient. For the greater is $\chi_{r'}$ in relation to the critical potential, the more abundant are the $(r' - 1)$ -fold ionized atoms which are chiefly effective in the absorption, and the increase in their number more than counterbalances the diminution in their mean absorbing power due to the restriction imposed by the higher $\chi_{r'}$ on the region of the spectrum for which they are available.

This is not the occasion to examine in detail the successive ionization potentials of the various elements, and their relation to the absorption of radiation at high temperatures, but it is clear that it is only a question of ascertaining these in order to be able to determine with precision the mean absorption coefficient, on the hypotheses introduced.

§ 19. Summary.

The paper is concerned with the evaluation of the absolute values of optical absorption coefficients. The word "optical" is to be understood as referring to the outer levels of an atom, though for highly-ionized atoms the corresponding frequencies may lie in the X-ray region.

The absolute values of monochromatic optical absorption

* Bohr and Coster, *Zeit. für Phys.* xii. p. 350 (1923).

† Compare Eggert, *Phys. Zeit.* xx. p. 570 (1919); Seares, *Astrophys. Journ.* lv. p. 227 (1922).

coefficients for neutral or once-ionized atoms appear to be of the order of magnitude of 10^9 , (§ 1), but little is known concerning them either experimentally or theoretically. A method of calculating them is furnished by Einstein's discussion of the thermodynamic equilibrium subsisting between a gas and black radiation in an enclosure. This provides a relation between the absorption coefficient and the mean time of occupancy of an outer orbit, the order of magnitude of which is known experimentally. It is shown, however, that the relation involves the unknown theoretical width of the "monochromatic" line (§ 5), and is therefore not available for precise estimates. But it provides confirmation of the order of magnitude of the absorption coefficients (§ 6).

Einstein's method can be applied to any condition of equilibrium to determine a relation between the "reaction-velocities" of the opposing processes (§ 4). In §§ 8-11 it is so applied to obtain the relation between photo-electric ionization and the probability of electron-capture by an ion, considering the equilibrium subsisting between atoms, ions, electrons, and radiation in an enclosure. For strict thermodynamic equilibrium it is found necessary to assume that electron-capture can be stimulated by external radiation (§ 9). The relation found evaluates the absorption coefficient for the region of continuous absorption lying on the high-frequency side of the limit of an optical series, in terms of the capture-probability function.

It is shown that for small speeds the probability of capture must vary inversely as the square of the velocity (§ 12). In so far as this holds exactly, the absorption coefficient beyond the series limit will vary as the inverse square of the frequency (§ 14).

The capture law used by Eddington for the interior of a star, where the mean absorption coefficient is of the order of 40 and the frequencies are in the X-ray region, is an inverse square law. Applied to hydrogen, calcium, and mercury by means of the formulæ obtained in the paper, it furnishes absorption coefficients in the optical region for the continuous spectrum beyond a series limit which are in agreement with the estimates of the monochromatic absorption coefficients already mentioned (§ 13). This gives some confirmation of the inverse square law over a considerable range of velocities; it may be considered as linking up the physics of the interior of a star, the physics of stellar atmospheres, and the physics of the atom.

The mean life of a hydrogen atom in the 2-quantum state, under the conditions of a typical stellar atmosphere, is shown

to be about 10^{-8} second, as limited by the process of photo-electric ionization (§ 15).

The mean absorption coefficient for a highly-ionized gas at high temperatures is determined (§ 16) ; it differs from Eddington's formula by a factor depending on the relevant ionization potentials (§§ 17, 18). The order of magnitude of these is determined as a function of pressure and temperature, and it is shown, for example, that under typical conditions in the interior of a star, atoms of iron will have lost their L-electrons but will mostly retain their two K-electrons.

The validity of the method and of the resulting formulæ is shown to be entirely independent of the extent to which ionization occurs by collision (§§ 4, 17).

I am grateful for the many opportunities I have had of discussing the foregoing paper with Mr. R. H. Fowler.

12th November, 1923.

*XIX. Note on an important Property of the
Auto-Transformer. By W. H. INGRAM, B.Sc.**

THERE are two methods of attacking the problem of the electrical transformer: the differential equation method, which goes back to Maxwell, and the "symbolic" method, due to Dr. Hopkinson †. The symbolic method presupposes simple sinusoidal potentials, fluxes, and currents (thus ignoring transients), but is applicable in cases where one or more of these quantities is not strictly sinusoidal by the simple fiction of "effective" circuit constants to give results to check with readings of wattmeters, etc., without regard to what the actual values of these constants are for the various Fourier components of the non-sinusoidal quantities in question. The symbolic method consists of a complex algebra of the relations among a system of radially-arranged vectors in a plane with reference to an associated coordinate system, the whole being conceived as steadily rotating, so that the projections of the said vectors on a reference-line in the plane give the sinusoidal variations in the quantities which the vectors represent. By neither

* Communicated by the Author.

† Given in a paper read before the Royal Society, March 10, 1887.

method, heretofore, has the transformer problem been solved in the sense of showing how all the electrical constants (effective or actual) of a transformer can be measured or calculated, or, as a matter of fact, any of them precisely, and it is the purpose of this note to show how all the electrical constants of a transformer may be *precisely* calculated on data from certain measurements and, moreover, for *any* condition of operation.

The data on a transformer essential to a precise calculation of its behaviour in operation are: its effective turns-ratio, effective winding resistances and leakage reactances, and excitation. All of these quantities are approximately determinable by well-known methods which give results sufficiently accurate for ordinary power circuits*, but it has been found that in circuits such as occur in telephone practice, where a transformer is often required at different times to operate under different impressed voltages and frequencies, the ordinary measurements of the quantities in question are insufficiently exact when used for predicting the behaviour of the transformer under abnormal conditions of excitation.

The crux of the problem lies in the handling of the core-losses, which may be thought of as occurring in a circuit linked to the working flux and of such impedance that the resistance part results in a power-loss corresponding to the hysteresis and eddy-current losses in the core, and such that the reactance part thereof consumes the wattless e.m.f. of excitation. If the coupling-ratio be taken as unity, such a system is the equivalent to the usual net† in which the core-losses are considered as taking place in a conductance and the magnetizing current as carried by a susceptance in a branch parallel to the conductance. The coupled-circuit equivalent, however, has an advantage of generality, being applicable in such cases as that of the auto-transformer, which admits of no equivalent conducting net.

A formula for the secondary-terminal potential of an auto-transformer is easily obtained on the assumption of the coupled excitation-circuit, and in the case of the step-down auto-transformer, or compensator, presents a novel property. Consider such a compensator having $n_1 + n_2$ primary and n_2 secondary effective turns and imagine the exciting circuit

* See Agnew and Silsbee, Bull. of Bureau of Stds., vol. x. (1914).

† Cf. Russell, 'Alternating Currents,' vol. ii. chap. xii.; and Steinmetz, 'Alternating Current Phenomena,' chap. xvii.

to have an impedance Z_0 and to be linked by n_0 effective turns to the working flux. Let the impedances of the two windings be Z_1 and Z_2 , said impedances being made up of the effective resistances and leakage reactances associated with their respective windings. The usual magnetomotive-force, current, and electromotive-force requirements give :

$$\left. \begin{aligned} n_1 i_1 + n_2 i_2 &= n_0 i_0, \\ i_1 &= i_2 + i_a, \\ e_1/n_1 &= e_2/n_2, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and, as a definition of Z_0 :

$$i_0 = \frac{1}{Z_0} \frac{n_0}{n_1 + n_2} (e_1 + e_2), \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where e_1 and e_2 are the internal e.m.f.'s (that part of the applied voltage E_1 which cancels the counter e.m.f. produced by the working flux). From (1) and (1a) and the equations

$$\left. \begin{aligned} E_1 &= i_1 Z_1 + E_a + e_1 \\ E_a &= i_2 Z_2 + e_2 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

it is easy to derive the formula for the secondary voltage E_a :

$$E_a = \frac{n_2}{n_1 + n_2} E_1 - \frac{n_0(n_2 Z_1 - n_1 Z_2)}{(n_1 + n_2)^2} i_0 - \frac{n_2^2 Z_1 + n_1^2 Z_2}{(n_1 + n_2)^2} i_a, \quad (3)$$

an inspection of which shows that when $n_1 Z_2 = n_2 Z_1$, the secondary terminal potential of the compensator will be independent of the exciting current. The E 's and i 's are vectors and the Z 's operators*.

Now, it is possible to connect up a transformer as a compensator, and with suitable loads and applied voltages to have exactly the same currents circulating in the coils in one case as in the other. This is so because there is no restriction on the direction of i_2 (with reference to the coordinate system mentioned in the first paragraph, or to the flux vector) as there is for the current in the secondary of a transformer.

* The secondary terminal potential of a step-up auto-transformer is given by :

$$E_a = \frac{n_1 + n_2}{n_1} E_1 - \left(\frac{n_2^2 Z_1 + n_1^2 Z_2}{n_1^2} \right) i_a - \frac{n_0}{n_1} \cdot \frac{n_2}{n_1} Z_1 i_0.$$

If we put $n_0 = n_1$ for simplification and let $\rho = n_1/n_2$, the impedance Z_t of a transformer with a secondary load Z_e is easily found to be

$$Z_t = \frac{\rho^2(Z_e + Z_2)Z_0}{Z_0 + \rho^2(Z_e + Z_2)} + Z_1, \quad . \quad . \quad . \quad (4)$$

and, of course, is a measurable quantity. Impedances z' and z'' in series the coils n_1 and n_2 may be introduced when the coils are connected as an auto-transformer and the relation

$$n_1(Z_2 + z'') = n_2(Z_1 + z') \quad . \quad . \quad . \quad (5)$$

experimentally established by adjusting z' and z'' until the secondary terminal voltage of the auto-transformer remains invariant under changes in the exciting current, which changes may be produced by superimposing small voltaic current on the alternating, or closing and opening the circuit of a loop or more of conductor linking the core. The impedance of the auto-transformer Z_s with the impedances z' and z'' connected in and with load Z_a is given by :

$$Z_s = \frac{Z_0[(1+\rho)^2 Z_a + \rho^2(Z_2 + z'') + (Z_1 + z')] + \rho^2 Z_a(Z_1 + z' + Z_2 + z'') + \rho^2(Z_1 + z')(Z_2 + z'')}{Z_0 + \rho^2(Z_2 + z'' + Z_a)}, \quad (6)$$

and may be measured.

The effective turns-ratio ρ may be obtained by a special test using (5) by letting z' and z'' be simple resistances, r' and r'' large enough so that, if either of a pair of values give the same ratio, either pair may be used to give ρ from the approximation $\rho = (R' + r')/(R'' + r'')$, where R' and R'' are the resistances of the coils n_1 and n_2 respectively as given by direct-current measurements. The equations (4), (5), and (6) are formally sufficient to give the remaining unknowns Z_1 , Z_2 , and Z_0 , but the latter must be really the same in all measurements, a condition which will obtain if the currents flowing in the coils are exactly the same. The load Z_a must be of such a magnitude that the current i_a will be equal to $(1 + n_2/n_1)i_2 + i_0$ (vectorially), where i_2 is the current in the transformer secondary during the measurement of Z_t and i_0 is the exciting current for the transformer primary for the operating voltage thereof, which also must be kept constant.

Solving for Z_0 and Z_1 (or Z_2) from (4) and (5) and substituting in (6) gives a cubic equation in Z_2 (or Z_1). If Z_0 is known to be comparatively large, as is the case in efficient transformers, (4) reduces to $Z_t = \rho^2(Z_e + Z_2) + Z_1$ approximately, and Z_1 and Z_2 may very easily be calculated using (5) and thereafter Z_0 calculated from (4).

A question which suggests itself is in regard to the effect of z' and z'' on the current wave-form and hence on the quantities to be measured. A qualitative answer to this problem may be obtainable when sufficient experimentation with the formulas of this note has been done, but at present it can only be said that when there is a comparatively large resistance in the generator circuit the current wave-form will be practically that of the voltage wave-form, and will be uninfluenced by small impedance variations in the transformer circuit.

Synopsis.

Voltage formulas are given for the auto-transformer and a method for measuring the leakage-fluxes, effective resistances, exciting impedance, and effective turns-ratio of a transformer.

Massachusetts Institute of Technology.

XX. *The Emission of Secondary Electrons from Metals under Electronic Bombardment.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

IN the *Philosophical Magazine* for May 1923, Mr. E. W. B. Gill criticized our interpretation of the results of a series of experiments which we made in the course of an investigation of the effects of electron collisions with platinum and with hydrogen. Mr. Gill had recently performed some experiments with a view to investigating the emission of secondary electrons from nickel, but found that the apparatus he employed (a Marconi M. T. 5 thermionic valve) was unsuitable for obtaining information with regard to the critical voltage at which the secondary emission begins, or the maximum velocity with which the secondary electrons are emitted from the metal. His criticisms of the way in which we interpreted our results were based on the assumption

that the apparatus we had used suffered from defects similar to those of his own apparatus. We replied to this criticism in your issue of July 1923, pointing out that the difficulties experienced by Mr. Gill were not encountered by us because our apparatus and method of experiment were designed to render the disturbing effects sufficiently small to be negligible in comparison with the effect under investigation.

In his criticism Mr. Gill attributed the falling-off of the number of secondary electrons leaving our bombarded platinum plate while this was still about 5 volts negative to the grid, to inadequate shielding of the plate by the grid. We showed in our reply that this could not have been the case, and in the current number of your Magazine Mr. Gill withdraws his contention, but returns to the attack along other lines. The tone of his criticism suggests that Mr. Gill thinks we ought to have performed the investigation using grid potentials up to 600 volts, as he did. It is difficult to see what useful purpose would be served by employing hundreds of volts on the grid when investigating a critical potential known to be less than 15 volts, especially as it is to be anticipated that the relative importance of the disturbing effects in comparison with the effect under investigation is likely to increase with the employment of large voltages. In the course of his letter Mr. Gill states:—"Prof. Horton and Dr. Davies used only one value of V_G , and deduced from a bend in their curve that secondary emission commenced for a velocity of impact corresponding to a potential drop of about 10 volts."

The description of our experiments (Proc. Roy. Soc. A, vol. xevii, p. 23, 1920) gives no justification for the statement that we used only one value of V_G . It is clearly indicated that observations were taken with different arrangements of the various electric fields, and it is expressly stated that our difference of potential V_2 (which controls V_G the difference of potential between the grid and the filament) was varied. Moreover, what we actually deduced from our curves was that an abrupt change in the rate of increase of the secondary current with increasing velocity of the primary stream commenced at an applied potential difference of between 10 and 11 volts, a result which we interpreted as supporting the view of other workers that the excitation of secondary emission (as distinct from reflexion of the primary electrons) required an applied potential difference between these limits. We explained that a correction

must be added to this applied potential difference to give the voltage equivalent of the velocity of impact of the primary electrons on the plate. The critical velocity of impact was that corresponding to a potential difference of about 13 volts.

Mr. Gill quotes one of our statements almost correctly. The statement is as follows:—

“The proof that the shielding action of the grid was almost perfect disposes of Mr. Gill’s contention that, because the authors made no allowance for an increase, with increasing plate potential, of the primary current to the plate at the expense of the primary current to the grid, their estimate of about 9 volts as the equivalent velocity of emission of the fastest secondary electrons is unreliable, and its agreement with the results of Lenard and others accidental.”

He goes on to remark, however:—

“The above statement of Prof. Horton and Dr. Davies appears to imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate, since they say that my contention that this occurs is disposed of.”

It will be seen that what we claim to have disposed of is Mr. Gill’s contention that our estimate of the velocity of emission of the fastest secondary electrons is unreliable. Our statement does not imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate; but we interpret the smallness of the downward slope of the part K of the curve reproduced in our paper as showing that, when the plate was 9 volts positive to the grid, this effect was negligibly small compared with the decrease which had occurred in the secondary emission from the plate.

The estimate of 9 volts as the maximum velocity of emission of the secondary electrons could only be considered unreliable if it could be shown that the current-potential difference curves from which it was obtained were a distortion of the true relations between the plate current and the electric field near the plate, such as would be obtained if the screening of the plate by the grid were very inadequate. As, however, it has been established that in our experiments the screening of the plate by the grid was almost perfect, it follows that the last-mentioned relations are correctly represented in the curve. Thus, there can be no doubt that the electric field in the neighbourhood of the plate at the stage when the steeply sloping portion, H, joins the part

K, which is almost parallel to the potential difference axis, is that due to the 9 volts which is then applied between the grid and the plate. If this junction of the two parts of the curve does *not* give a measure of the maximum velocity of the secondary electrons, then, either (a) the bend of a certain length of the curve immediately preceding 9 volts is to be attributed entirely to the variation of the primary electron current to the plate, or (b) in the part K of the curve above 9 volts, the current due to the secondary electrons is not of negligible magnitude, so that this part of the curve, which is nearly parallel to the potential-difference axis, is not an indication of the total primary current to the plate.

Now with regard to (a), an inspection of the curve shows that no appreciable length of the bend of the curve immediately below the 9-volts' point could possibly be due entirely to the variation of the primary plate current with the electric intensity near the plate, unless the curve were a considerable distortion of the relation between these quantities; and this we have shown is not the case. *Thus the maximum velocity of emission of the secondary electrons is not less than that equivalent to about 9 volts.*

With regard to (b), it follows from Mr. Gill's argument that, since the measured current remained almost constant as the potential difference between the grid and plate was increased beyond 9 volts, the primary plate current must either have attained an almost constant value at 9 volts, or must increase more rapidly with increasing plate potential than the measured current does in this part of the curve. In the event of the latter alternative occurring, the measured current could only remain practically constant if the secondary current increased at the same rate as the primary plate current. Such an occurrence is extremely improbable, since it would mean that when the potential difference between the grid and the plate is increased beyond 9 volts, the current carried by the secondary electrons leaving the plate suddenly begins to increase, instead of continuing to decrease, with increase of the field tending to prevent electrons leaving the plate.

If the primary plate current has attained its saturation value when the potential difference between the grid and the plate has reached 9 volts, then, since the actual measured current is practically independent of the subsequent increases of plate potential, it follows that the current

due to the secondary electrons leaving the plate must have attained a value which is constant within the limits detectable in our investigation—that is to say, it must have become independent of the velocity of impact of the bombarding electrons or of the resulting potential difference opposing the motion of the electrons from the plate to the grid. This result is readily explained if this constant value of the secondary current is zero, whereas whatever the origin of the secondary current it is difficult to see how, if this current is at all comparable with the primary plate current, it can be sensibly independent of the two factors mentioned above. It therefore appears that *there is no appreciable number of secondary electrons leaving the plate with velocities greater than that corresponding to a potential difference of about 9 volts.*

Thus the most reasonable interpretation of the junction of the parts H and K of the curve which occurs at about 9 volts is that secondary emission practically ceases at this stage because the velocity of emission of the fastest secondary electrons from platinum corresponds to a potential difference of this value.

We therefore maintain that our proof that the shielding action of the grid in our experiments was almost perfect has disposed of Mr. Gill's contention that our estimate of the velocity of emission of the fastest secondary electrons is unreliable. This estimate—like the other conclusions we drew from this series of experiments—is in general agreement with all the more recent work on the subject*.

* R. A. Millikan and I. G. Barber, *Proc. Nat. Acad. Sci.* vol. vii. p. 13 (1921); I. G. Barber, *Phys. Rev.* vol. xvii. p. 322 (1921); H. E. Farnsworth, *Proc. Nat. Acad. Sci.* vol. viii. p. 251 (1922), and *Phys. Rev.* vol. xx. p. 358 (1922); L. E. McAllister, *Phys. Rev.* vol. xxi. p. 122 (1923).

Royal Holloway College,
Englefield Green.
Nov. 10th, 1923.

Yours faithfully,
F. HORTON,
A. C. DAVIES.

XXI. *Notices respecting New Books.*

Life Movements in Plants. By Sir JAGADIS CHUNDER BOSE, Longmans, Green & Co., 1913. (Transactions Bose Institute. vols. iii. & iv., 1920, 1921.) 20s. net.

THIS volume continues the lines of inquiry pursued in the two volumes on *Life Movements in Plants* by the same author published in 1915 and 1919. The present work contains accounts of investigations on geotropism, on dia-heliotropic attitude of leaves as regulated by transmitted nervous impulse, on assimilatory and dissimilatory changes under light, on new methods of recording the effects of protoplasmic changes under stimulus, and also of various methods and appliances for detection of the two fundamental reactions to which all plant movements are due. The important work done by Sir J. C. Bose is well known. This new series of researches is of great value, and will command the attention of all those who are concerned with the application of physical methods to biological phenomena.

Dynamics. By HORACE LAMB, Sc.D., LL.D., F.R.S. 2nd Edition. (Pp. xi+351, with 93 figures.) (Cambridge: at the University Press, 1923. Price 12s. 6d. net.)

THE first edition of this well-known text-book was published in 1914. It is a tribute to its excellence that in the new edition no alterations have been found necessary beyond the correction of a few errors, chiefly in the examples, and the re-writing of a few pages. Detailed notice of this edition is therefore unnecessary. It is worthy of mention that the price for the new edition has been reduced from 17s. 6d. net to 12s. 6d. net. It is very desirable that the price of books which are suitable for extensive use as text-books should be kept as low as possible, and it is to be hoped that the substantial reduction in the price of the present edition will make it accessible to a much greater number of students.

The Properties of Matter. By BASIL C. McEWEN, M.C., B.Sc. Professor of Science and Vice-Principal of His Exalted Highness The Nizam's College, Hyderabad, India. (Pp. vii+316, with 137 figures.) (London: Longmans, Green & Co., 1923. Price 10s. 6d. net.)

THE majority of text-books dealing with the Properties of Matter commence with a study of matter in the solid state and then proceed to the consideration of liquids and gases. In this way matter in its most complex form is studied first. In the present work the reverse order is followed, and this procedure has

much to recommend it. The standard is that of the B.A. and B.Sc. pass degrees. A noteworthy feature of the book is that, in addition to the theory of the subject, a number of experiments are described which the student can perform himself, and which will help to give him a better appreciation of the subject. It is advisable in this as in other branches of physics, that the practical and theoretical study should proceed together.

One peculiarity which strikes us in the treatment is that, although a chapter is devoted to the first law of thermodynamics no mention is made of the second law, which is, nevertheless, applied without explanation to such matters as the change of boiling and freezing points with pressure. We would suggest that in a second edition a short account of the second law should be incorporated.

The treatment of the various subjects touched upon follows conventional lines. Only an elementary knowledge of mathematics is assumed, and results whose derivation would require a more extensive knowledge, such as the rate of fall of a small sphere in viscous fluid, are given without proof. The text-book can be recommended for an elementary and comprehensive treatment of the properties of matter as far as the standard required for a University pass degree.

L'Evolution des Etoiles. By JEAN BOSLER, Director of the Marseilles Observatory. (Pp. 103, with 19 figures.) (Paris: Les Presses Universitaires de France, 1923. 10 f. net.)

THIS volume contains a concise and readable account of our present state of knowledge on the subject of the evolution of stars. Much of the original work which is summarised in it has only been published within the last few years, and it is valuable to have it collected together and arranged in logical sequence in such a volume as the present.

The classification of stars by their spectra is dealt with first. It was the progressive sequence into which stellar spectra could be classified which provided the basis for the initial theories of stellar evolution. For a time there were two rival theories: the one requiring an order of evolution commencing with the blue stars and proceeding through those of solar type to the red stars; the other required a two-branched order, commencing with red stars of low density and proceeding with rising temperature to blue stars, whence the sequence continued with decreasing temperature to red stars of high density. In this connexion the various methods by which the temperatures of stars have been determined are described.

An account is then given of the recent work of Saha, which has had such remarkable success in explaining the main features of stellar spectra, as due to ionization as a function of temperature and pressure. From a consideration of the appearance and disappearance of various lines, the approximate temperatures of

each type can be determined: these temperatures agree reasonably well with those obtained by observation.

The giant and dwarf theory of stars is led up to by a consideration of the spectroscopic method of determining stellar parallaxes, and of the results so obtained for the absolute luminosities of stars. It is shown that red stars may be divided into two groups of high and low luminosity, and that there are no blue stars of low intrinsic luminosity. An account of Russell's theory of evolution is then given. The relationship of this theory to the masses of the stars is considered, and it is shown that equipartition of energy obtains approximately for stars of different mass.

The general course of evolution having thus been indicated by the results of observation, the theoretical discussion of the same problem follows naturally. A fairly detailed account of the theory of radiative equilibrium is given. This theory, applied to giant stars, has had remarkable success in explaining the results of observation, and has also been successful in providing a general explanation of the phenomena shown by dwarf stars. It accounts also for the fact that the masses of stars are compressed within somewhat narrow limits; the temperature of stars of very small mass will never increase sufficiently for them to become visible, whilst very large masses would be blown asunder by the pressure of radiation.

Finally, the problem of the origin of the heat of the stars is considered.

Although the treatment in general is accurate and remarkably clear, there are one or two statements which are somewhat misleading. On p. 29, the agreement between the observed and calculated diameters of Betelgeuse is quoted as evidence that the stars radiate like black bodies. This agreement, of course, affords no evidence in the case of dwarf stars, which certainly do not radiate like black bodies. On p. 50, the remarks in reference to the relative numbers of stellar parallaxes determined by the trigonometrical and the spectroscopic methods do not state the case fairly. The spectroscopic results are based entirely upon the trigonometrical; moreover, the former for certain statistical purposes are of comparatively little value owing to the systematic dependence on the masses of the stars which has recently been pointed out. No mention of this dependence is made.

The New Physics: Lectures for Laymen and Others. By ARTHUR HAAS, Ph.D., Professor of Physics in the University of Leipzig. Translated by R. W. LAWSON, D.Sc. (Pp. xi+165, with 7 figures.) (London: Methuen & Co., 1923. Price 6s. net.)

Recent Developments in Atomic Theory. By LEO GRAETZ, Professor of Physics in the University of Munich. Translated by GUY BARR, B.A., D.Sc. (Pp. xi+174, with 39 figures.) (London: Methuen & Co., 1923. Price 9s. net.)

THESE two volumes both deal in a readable, non-technical manner

with some of the more important of the many recent striking developments of physics. The first one covers the wider ground. Commencing with an account of Maxwell's electromagnetic theory of light, a chapter on molecular statistics follows. These two lead naturally to the extension of Maxwell's theory by Lorentz, in his electron theory. The consideration of the structure of matter and of the quantum theory follow. The application of the latter has enabled the electron theory to be extended to cases in which the laws of classical mechanics failed to provide a satisfactory explanation. In particular, as developed by Bohr and others, it has enabled the spectrum of hydrogen to be accounted for, the fine structure of spectral lines and the arrangement of the elements into a periodic system. These matters are all dealt with in a lucid manner. The closing chapter deals with the theory of relativity, which in the hands of Einstein has completed the work of Maxwell and Lorentz, and provided an explanation of the phenomena of gravitation. The volume thus contains in brief compass an account of the most important developments of physics of recent years, written in a simple style suitable for the average intelligent layman.

The second volume deals more particularly with the recent work which has led to our present knowledge of the structure of the atom. Its publication has followed closely upon Professor Rutherford's presidential address at the last meeting of the British Association. The broadcasting of that address has stimulated many laymen with a desire to obtain further information with regard to this subject, in the development of which Rutherford has taken such an important part. This volume can confidently be recommended for this purpose. It starts with an account of the atomic theory in chemistry and in physics, and the use of statistical methods for the kinetic theory of gases. An account of ions in electrolysis leads to the conception of the atom of electricity, and so to the electron, and the phenomena of electrical discharges through gases. An account of radioactive phenomena follows, including Wilson's work which suggested Rutherford's theory of the atom. This is considered in conjunction with Aston's work on isotopes. Further support is given to the theory by X-ray spectra and the work of Moseley and others. An account then follows of line spectra and Bohr's model of the atom and of the extensive developments which have followed upon the application of the quantum theory. It thus provides a very complete but at the same time easily intelligible account of the present state of knowledge in this important branch of physics.

In conclusion, it may be added that the translators have in each case performed their task admirably.

XXII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlv. p. 1026.]

November 7th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

THE following communication was read:—

‘The Igneous Rocks of the Tortworth Inlier.’ By Prof. Sidney Hugh Reynolds, M.A., Sc.D., F.G.S.

The igneous rocks of the Tortworth Inlier were described by Prof. C. Lloyd Morgan and the author in a paper published in the *Quarterly Journal* of this Society in 1901 (vol. lvii. p. 267). The present paper contains information which has become available since the publication of that just cited. The igneous rocks occur in two bands, the upper of which is associated with calcareous tuffs containing Silurian fossils and is doubtless lava. The lower band was also regarded as a lava in 1901, but it now seems probable that it is intrusive. The rocks of the two bands, though showing well-marked differences, have several features in common. In each case the feldspars, although doubtless originally labradorite, are now wholly or partly in the condition of albite or oligoclase. In each case pyroxene is present only in the form of very small crystals, is relatively scanty, and predominantly rhombic. The rocks of the lower band are characterized by the presence of pseudomorphs after olivine, and may be grouped as olivine-enstatite-basalts.

Those of the upper band are devoid of olivine, and consist of pyroxene-andesite. They are characterized by the presence of highly corroded xenocrysts of quartz and feldspar, and by the occurrence of variolitic and glassy patches in the ground-mass.

November 21st.—Prof. A. C. Seward, Sc.D., F.R.S.,
President, in the Chair.

The following communication was read:—

‘The Development of the Severn Valley in the Neighbourhood of Iron-Bridge and Bridgnorth.’ By Leonard Johnston Wills, M.A., Ph.D., F.G.S.; with a Section on the Upper Worfe Valley, in collaboration with Ernest Edward Leslie Dixon, B.Sc., F.G.S.

The investigation of the Iron-Bridge Gorge and the surrounding country was undertaken with the view of finding detailed evidence for or against the hypothesis of the origin of the gorge as a Glacial overflow-valley. This hypothesis was put forward independently by Charles Lapworth¹ and F. W. Harmer.² Its correctness has been borne out by the detailed evidence now presented.

¹ *Proc. Geol. Assoc.* vol. xv (1898) p. 425.

² *Q. J. G. S.* vol. lxiii (1907) pp. 477–81.

The area investigated is roughly delimited by the following localities:—Much Wenlock, Buildwas, Oakengates, Shifnal, Worfield, Hampton Loade, Morville. It can be subdivided physiographically into

- (a) The Buildwas area, a part of the Shropshire plain.
- (b) The Barrow-Broseley and Madeley-Shifnal plateau, bounded on the north-west by Wenlock and Benthall Edges, and the Wrekin; it stretches as a main watershed, except at Iron-Bridge, north-eastwards towards Shifnal and Newport (Salop). This plateau was the pre-Glacial watershed between the Dee-Mersey drainage and the Worfe, which was then an important feeder of the Worcestershire Stour.
- (c) The Worfe Vale, a mature valley.
- (d) The Iron-Bridge Gorge, and its less gorge-like continuation as the Severn Valley by Bridgnorth.

Detailed mapping of the drifts has shown, first, that the Buildwas area was as deeply eroded as now in pre-Glacial times; and, secondly, that a belief in the existence of the Iron-Bridge Gorge at that time is incompatible with the distribution of the drifts on the plateau above Iron-Bridge, with the youthful features of the gorge, and with the absence of Glacial deposits in it. Everything points to the gorge being of late-Glacial origin, and to the Worfe Vale having been formerly the main drainage-line on the south-east side of the plateau, which then formed an unbroken watershed.

Practically the whole district was under ice at the maximum of the north-western or Irish-Sea glaciation. When retreat began, the ice-sheet separated into two lobes that remained confluent in the north. The lobe north-west of the pre-Glacial watershed was pressed counter-drainage against it. Glacial lakes were thus formed. The other lobe, on the south-east side, persisted longer in the low ground of the Worfe Vale. Marginal drainage was of special importance here, being reinforced by overflows from the lakes across the divide.

Various stages in the retreat are sketched out, and their relation to the drift-outcrops and to the former lines of drainage is shown; it is also shown how the waters of the Glacial lakes, west and north of the watershed, escaped at different times over different cols.

One of these overflows is of especial importance in connexion with the origin of the Iron-Bridge Gorge: namely, the Lightmoor overflow, about a mile north of Iron-Bridge. This appears to have drained a lake in Coalbrookdale, and to have operated before the Iron-Bridge overflow began. It is necessary to postulate a slight re-advance of the ice to close this overflow, and thus raise the level of the lake until it flowed out over a higher col at Iron-Bridge. Evidence for this re-advance is given. Reasons are adduced for the immediate rapid erosion of the upper part of the Iron-Bridge Gorge to a level too low to allow the Lightmoor overflow to operate a second time on the renewed retreat of the ice.

Up to about this stage, the Worfe and its tributaries (one of which now became the Iron-Bridge Gorge) had been engaged in

clearing the drift out of their valleys, and in reducing the thalweg of the trunk river to a base-level. Hereafter deposition of the 'Main' Terrace of the Severn and of the terrace-like gravels of the Worfe commenced. An important overflow at Oakengates brought water from another lake on the northern side of the watershed at this stage. Some of the gravels of the Mad Brook, the Worfe, and the Wesley Brooks can be correlated with this overflow.

As the ice retreated farther, the Coalbrookdale Lake was so enlarged that it covered the Buildwas area. Sands and gravels were deposited in the lake (the Buildwas Sands). The level of the lake fell to about 300 feet O.D. as the outlet was lowered; but there is evidence that it remained at about this level for a long time, probably on account of the graded state of the Severn Valley below Iron-Bridge, of which we have evidence in the Main Terrace. This terrace can be traced right down the Severn, although evidence for this is not brought forward here. Its connexion with the north-western or Irish-Sea glaciation will, however, be important in studying the relation of the terraces (not only of the Severn, but of other rivers) to the Glacial Episodes.

Long after the initiation of the Iron-Bridge Gorge, ice still covered the upper Worfe Valley. Retreat-stages here have been made out largely through the collaboration of Mr. E. E. L. Dixon. When the ice retired to the north of the watershed hereabouts, Glacial Lake Newport came into being, and subsequently united with the Buildwas Lake on the retreat of the ice-front from the foot of the Wrekin. The outflow at Iron-Bridge thus increased, although the united lakes maintained the 300-foot level, mentioned above, for some time. The subsequent rejuvenation of the Severn below Iron-Bridge was probably brought about chiefly by an elevation of the whole land relative to the sea. Stages in this rejuvenation are marked by terraces.

In the Bridgnorth area the terraces are as follows:—

*Approximate height in feet of the
terrace-surface above the present
flood-plain of the Severn.*

Hoards Park-Eardington Terrace	150 to 125
Main Terrace.....	120 to 100
Upper Danesford Terrace	70 to 60
Lower Danesford Terrace	35 to 30

So far, only the Lower Danesford Terrace has been recognized both above and below the Iron-Bridge Gorge.